polymetron

Odour control in a municipal waste water treatment

application note

8810 analyzer

8350/8351 probe

9135 transmitter

zellweger analytics

1 - WHAT IS THE PROBLEM ?

Waste water treatment plants are integrated into different environments, built in cities, under football grounds fields or in buildings: none of these would be possible without an efficient odour treatment system.

Even in the industrial sector, different unpleasant odours are produced.

Industrial unpleasant odours

Industries	**Origin of odours**
Cement works, lime kilns	Acrolein, amines, mercaptans, ammonia, dibutyl sulphide, H_2S, SO_2, etc.
Pharmaceutical industries	Fermentation products
Food industries	Fermentation products
Food industries (fish)	Amines, sulphides, mercaptans
Rubber industries	Sulphide, mercaptans
Textile industries	Phenolic compounds
Paper pulp industries	H_2S, SO_2
Organic compost	Ammonia, sulphur compounds

Odour treatments

Odours emanating from water treatment plants are due to gases or fumes given off by some of the components of waste water. They are also caused by compounds formed during the various stages of treatment. The list of pollutants to be encountered in the atmosphere of a treatment plant includes many families of compounds based on nitrogen, sulphur, hydrocarbons etc.

Gas pollutants in waste water treatment plant

Nitrogen compounds	
Ammonia	NH_3
Amines	$R\text{-}NH_2$, $R_2\text{-}NH$, $R_3\text{-}N$
Amines oxides	$RH\text{-}NO$, $R_2H\text{-}NO$, $R_3\text{-}NO$

Nitrogen	NO_x
Sulphur compounds	
Hydrogen sulphide	H_2S
Mercaptans	R-S-H, R-S-R
Hydrocarbons	
Saturated and/or unsaturated	
Aromatic	
Chlorine derivatives	
Other compounds	
Aldehydes	R-CHO
Acrolein	CH_2-CHCHO
Alcohols	R-CH_2OH
Saturated and.or unsaturated fatty acids	
Skatole	
Diamino sulphides	R_2=N-S-N=R_2

2 - ODOUR TREATMENT PROCESS

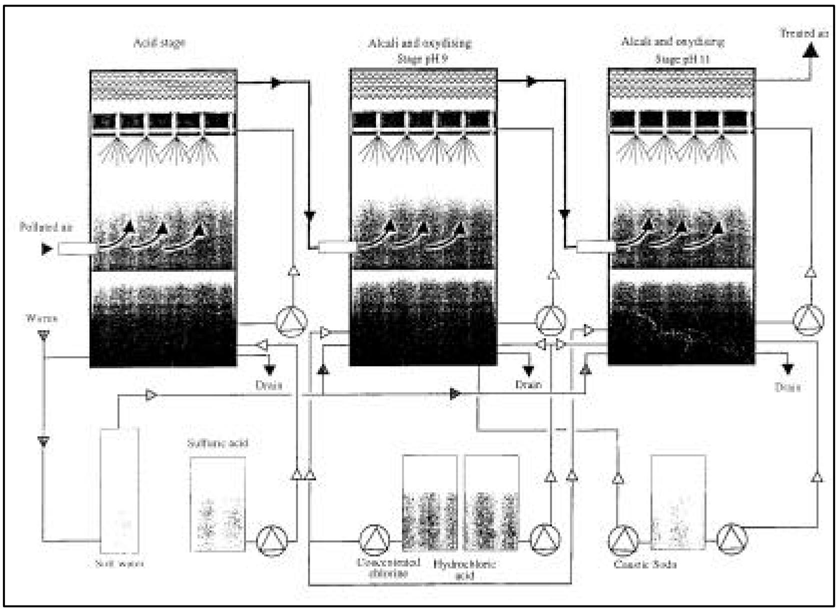


Figure 1

Odour treatment necessitates a few pre-treatment techniques (reducing emissions, ventilation etc) before the chemical treatment in a gas scrubber occurs.

The first step of the gas scrubber is to transfer pollutants from the gas phase to the liquid phase, sometimes enhanced by the second stage oxidation of the components in the liquid phase.

This single second stage often proves itself insufficient to remove a wide spectrum of odours. The solution lies in providing several stages in series. Major characteristics for this gas treatment are:

- a "stage column" filled with sulphuric acid solution, operates against the dust, cools gases and reduces ammonia and amine exhaust.
- a 'packed column' filled with sodium hypochlorite and caustic soda solution realises the oxidation of the compounds based on sulphur, nitrogen, oxygen and dissolved acid derivatives created previously.

<u>Examples of chlorine oxidation reactions</u>:

1)	NH_3 + HClO	=>	NH_2Cl (Chloramine)
explained by	$NH_3 + H_2O$	=>	$NH_4^+ + OH^-$
	NH_4^+ + HClO	=>	$NH_2Cl + H_3O^+$
2)	$H_2S + 4ClO_2^-$	=>	$4Cl^- + H_2S0_4$
3)	CH_3SH + 3ClO (Mercaptan)	=>	$CHH_3S0_3 + 3Cl^-$ (Methylsulphonic acid)

- the "packed column" is replenished thanks to a source of chlorine adapted to the consumption of chlorine per hour. For example, concentrated sodium hypochlorite, industrial sodium hypochlorite solution or electochlorinator. (See Figure 1)

In the "packed column", the content of chlorine (in its form ClO^-) corresponds with the oxidation reagent's reservoir against pollutants. The level of chlorine is dependent on:

- the average concentration of pollutant
- volume of air through the tower
- response time analysis - because with only one analysis per day, carried out by the laboratory, the user will be obliged to increase the injection of chlorine. This is why the level of chlorine sometimes ends up at 2g/l. Therefore, it will take at least one night to consume all the chlorine in the tower.

As a consequence, the consumption of chlorine per week becomes tremendous. This causes financial, transportation and stock problems.

If the waste water plant is small (below 50,000 m^3/h of treated toxic air), these problems of cost, stock and transport cannot be solved. However, costs can be reduced by using low-cost sodium hypochlorite, which is released, for example, by industrial manufacturing cleaning solutions. In this case, the source of chlorine is mixed with soap-like compounds which change the composition of the sample.

If the waste water plant is large, the source of chlorine becomes an electrochlorinator. Sodium hypochlorite is produced on site by electroxidation of chloride (Cl^-) in the gas chlorine (Cl_2) and electroreduction of water (H_2O)in hydrogen gas, mixed with hydroxyl ion (OH^-).

This technique means the customer has to deal with electrochlorination, but reduces the cost of the raw product (sodium chloride salt and electricity). In this case, together with chlorine comes small graphite (carbon) particles from electrode decomposition. These particles also change the sample composition.

3 - ON-LINE CHLORINE MEASUREMENT

3.1 Continuous chlorine measurement: why ?.

Maintaining the correct content of chlorine in the water is the key to a good process. Optimizing the injection of chlorine will reduce the cost and will guarantee at any moment that the process is within specifications for pollutant-free exhaust.

3.2 Chemical description of the sample:

Chlorine	100-2000 mg/l depending on the NaClO injection
Alkalinity	8<pH<11 depending on the NaOH injection
Hardness	TH<10° French Degree if make up water is decarbonated

3.3 Review of the available measurement technologies

** Potentiometric measurement*

The oxidoreduction potential measurement of the solution is sometimes proposed because it's cheap. We must insist that redox potentials have nothing to do with the concentration of chlorine in the water. At most, it indicates if one oxidizing reagent is in excess or not, according to the formula:

$$E = E_0 + \frac{K}{n} + \frac{\log (\text{oxidized form})}{(\text{Reduced form})}$$

E is then dependent on all the different species combined in the solution, and reflects only the ratio between the oxidized and the reduced form. Therefore, operating with the redox or RH measurement will be risky if there is not a large excess of chlorine in the bath. Oxidizing towers equiped with redox measurement will consume a lot of concentrated chlorine solution. The bigger the station, the more the chlorine waste will increase costs, stock and transport problems. This therefore is not the ideal solution to control the process.

** UV Measurement:*

Today, there are no industrial analysers based on this principle for this application, because complex sample contents cause too much interference on the UV detection.

** Amperometric measurement:*

Amperometry analysis follows the reduction current between the two electrodes which is proportional to the concentration of the oxidizing reagent.

This is the principle of the CHLOROMAT for drinking water. Three years ago Polymetron released a high concentration chlorine system on the French market with:

- a dilution of the sample to reduce the reduction wave

- an acidification of the diluted sample

- a CHLOROMAT cell and the transmitter

Its use on the site has shown this is a good solution but with the following drawbacks:

- concentration of NAOH can change a lot in a very short time, taking away the pH buffered value

- source of chlorine e.g. electrochlorinator will bring particles which require maintenance on the analyser itself or on a filtration unit

- source of chlorine e.g. industrial cleaning solution is mixed with foam and detergent which are not suitable for the analysis

3.4 - Potentiometric titration

3.4.1 Measurement principle

This measurement determines the chlorine concentration by the quantity of thiosulphate oxidized by the chlorine present in the sample.

In principle (equation N°1l):

Cl_2	+	$2(S_20_3^{2}\ )$	=>	$2Cl^-$ +	$S_4O_6^{2-}$
Chlorine gas	Thiosulphate			Chloride	Tetrathiorate

But in the water at pH=5, chlorine gas produces (equation number 2):

$Cl_2 + H_2O$ =>	HClO	+	HCl
Chlorine	Hypochlorous acid		Hydrochloric acid

(Equation N°1 +Equation N°2) leads to thiosulphate oxidation in water at pH3

Equation N°3: $2HClO + 2H^+ + 2(S_2O_3^{2-})$ => $2Cl^- + S_4O_6^{2-} + 2H_3O^+$

3.4.2 Laboratory measurement

Potential changes in the manual titration can be observed on a platinum electrode or with changes in the colour of an indicator. The common indicator is named thiodene and corresponds with a soluble amidon version.

(Equation no4): $2HClO$ + $2H^+ + KI$ => $I_2 + KCl + H_20$
(Equation no5): I2 + 2 Thiodene $2I^-$ + S_4O^{2-}
iodine thiosulphate iodide
Tetrathionate

Thus every single molecule of chlorine is transferred into iodine (equation N°4). The iodine molecules react as an oxidant over the thiosulphate (equation N°5).
When the blue colour of the indicator disappears, it means that all iodine has disappeared in the reaction with the thiosulphate. Thus, the volume of thiosulphate added to the solution is proportional with the original chlorine concentration.

3.4.3 8810 Analyser for chlorine measurement in that application

**** Methodology***

Titration as follows:

. Sample taken: 70ml

. pH sample conditioning with 4ml of acetic acid buffer solution

. Thiosulphate solution added until redox potential shows that chlorine has disappeared. Proper working time of the titration pump is related to the original chlorine concentration by a calibration curve.

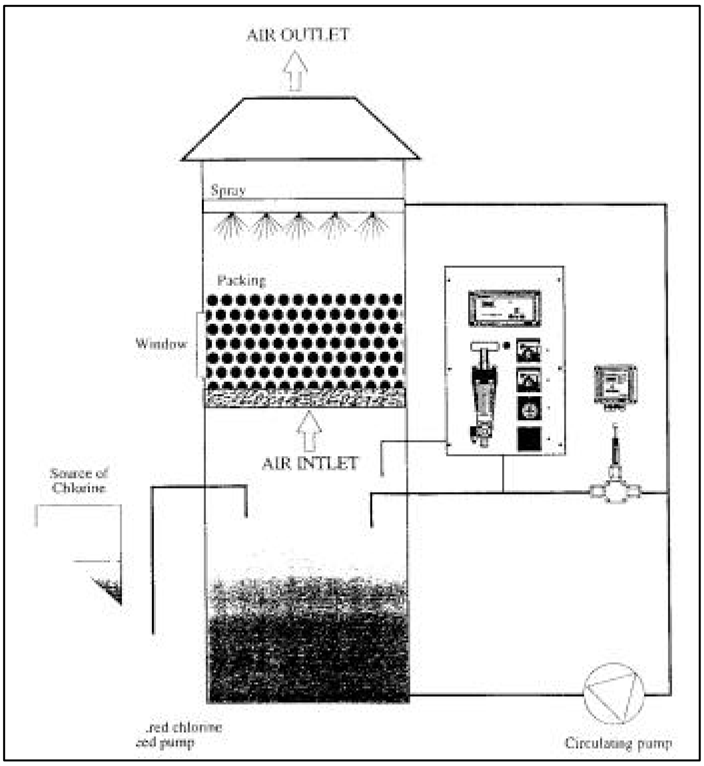
. Chemical cleaning phase programmable in frequency, length and strength.

In other words, the principle and operations of the 8810 titration are exactly the same as the principle and operations of laboratory titration. In fact, for many people, this likeness between the laboratory and 8810 titrations creates a strong feeling of confidence. This is one of our major sales argument.

**** 8810 analyser installation***

. Insert 8810 after the circulating pump of the bath
. Request a fast loop for the sample line

- Freely programmable alarm for low and high concentrations



**** System configuration***

.	368810,20xxx	8810 ORP analyser complete with platinum and reference electrode and one peristaltic pump for titration with sodium thiosulfate
or		
	368810,50xxx	Same analyser with a piston pump instead of a peristaltic pump
.	368810,700xx	Additional peristaltic pump for conditioning with acetic acid / acetate buffer
or		
	368810,71050	Additional piston pump for conditioning instead of a peristaltic pump
.	368810,56000	Chemical cleaning complete with 10 l canister and level detector

OPTIONS :

- 368810,40000 Polyester wall mounting cabinet
- 368810,45000 Free standing cabinet

N.B. Automatic calibration doesn't exist for this application. Chlorine solutions are not stable enough in time (NaClO slowly transformed to Cl_2 under oxygen activity).

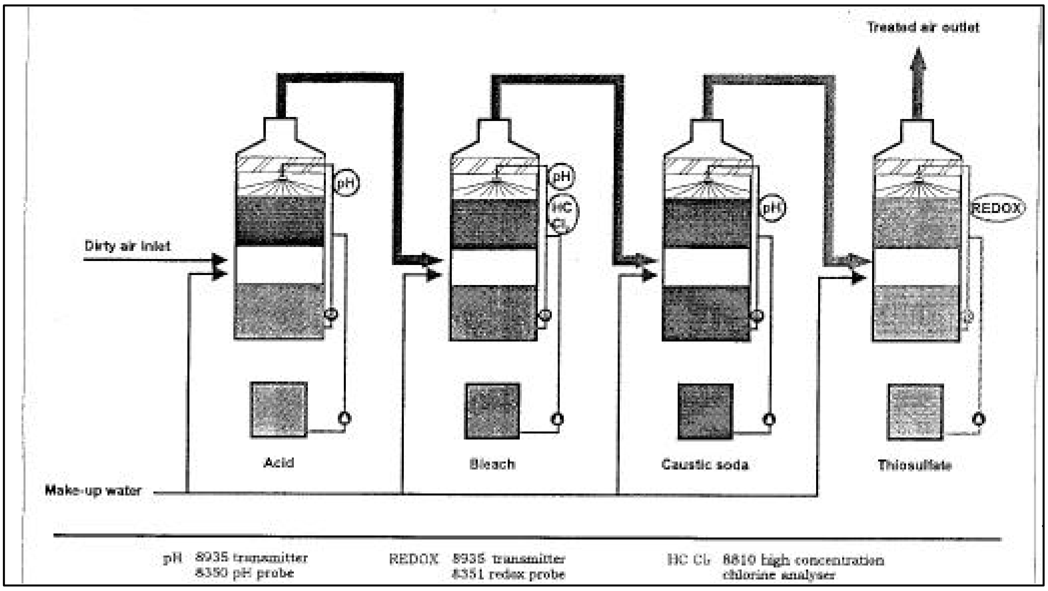
**** Main sales arguments / benefits of this solution***

- 8810 measurement principle is the same as laboratory one
- 8810 measurement operation is the same as laboratory one
- Continuous measurement of the residual chlorine guarantees the correct oxidation of the gas pollutant. It's then possible to reduce the residual chlorine average concentration. Chlorine chemical product consumption can be reduced by more than factor 3 !
- If the addition of the chlorine is controlled, the amount added, stocked and transported is reduced. Regarding chlorine, you are immediately on the road to a safer world.

4. pH AND REDOX MEASUREMENT

As described on the above drawing on-line CHLORINE measurement is a key factor to manage this odour control process successfully.

However, pH is vital to monitor on-line and to a lesser extent Redox potential.



4.1 Why pH and Redox measurement ?

- In the acid stage to ensure that the pH is within specifications and control directly the sulphuric acid addition

- In the alkali and oxidizing stage to ensure the pH is within specifications (~ pH9) and control directly the caustic soda and hydrochloric acid pumps

- After the last oxidizing stage, sodium thiosulfate could be added to reduce the excess of chlorine. If such a neutralization is applied an easy and efficient way to add the right amount of sodium thiosulfate is to monitor the Redox potential to control directly its addition.

4.2 System configuration

*** pH loop***

. 09135=A=0000	9135 single channel pH/ORP transmitter
. 08350=A=0000	8350 combination pH probe with 10 m high impedance cable
. 08350=A=2000	Flow-through chamber in PP
. 08350=A=2010	Connecting tube in PVC

*** ORP loop**

. 09135=A=0000	9135 single channel pH/ORP transmitter
. 08351=A=0000	8351 redox sensor with 10m cable
. 08350=A=2000	Flow-through chamber in PP
. 08350=A=2010	Connecting tube in PVC