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AN AMMONIA MONITOR FOR THE WATER INDUSTRY

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HISTORICAL BACKGROUND

Following the emergence of the European Community as a unified trading and economic entity, the various member states are required to follow certain directives governing their social affairs. Many of these directives concern the quality of the air we breathe, and the water that we use for consumption or in industrial processes. In order to comply with these directives a major overhaul of the water industry in the UK was required. For example, in many coastal towns and resorts there has never been any formal sewage treatment since, traditionally, all waste was dumped at sea through outfall pipes. Because this is no longer acceptable, whole new treatment systems are required.

CURRENT ORGANIZATION OF THE UK WATER INDUSTRY

For reasons which one can probably surmise, the first part of this overhaul was to privatize the industry. This consisted of creating ten individual Water Authorities according to geographical location within England and Wales with separate Authorities for Scotland and Northern Ireland. Each authority is responsible for the supply of drinking water and water for domestic and industrial consumption, and the treatment of all wastewaters, to the required standards laid down by both UK legislation and the appropriate EC directives. Compliance is monitored by the National Rivers Authority which has overall responsibility for all the freshwater supplies in the UK. The financial side of the industry is monitored on behalf of the consumer by OFWAT a quasi-government organization or Quango, which has the power to limit the water rates charged by the individual Authorities.

COST REDUCTION AND REMOTE MONITORING

The ten UK Water Authorities are autonomous companies listed on the UK stock exchange. They currently face a difficult time in undertaking a huge capital investment programme to update entire systems, and demonstrate compliance with legislative requirements, while being limited in the price increases that they can pass on to the consumer. Part of the solution is to increase efficiency and reduce costs, the latter inevitably entailing manpower reduction. The intention is to reduce manpower by automating treatment processes and monitoring them remotely from a central system.

In order to automate a process it is necessary to control it; in order to exercise control the process has to be monitored, and in order to monitor certain fundamental measurements are required. In order to make these measurements, it is essential that the critical variables are known, and that there exists a reliable means of measuring each of these variables which is amenable to long term unattended operation, and can be interrogated remotely. A considerable number of drinking water treatment facilities have been essentially unmanned for many years, but large sewage treatment works have not, and this is where the first serious look at demanning is taking place.

SEWAGE TREATMENT

The first task is to identify the critical parameters in the sewage treatment process. Sewage is the waste waters and excreta of both domestic and industrial processes, and is an undefined, complex mixture of chemical and biological components. It is a highly turbid liquid, greyish in color, which normally putrefies quickly using up any dissolved oxygen. The treatment of sewage must convert this mixture to relatively clean water prior to returning it to the freshwater system.

The first stage involves removal of large solid objects, and grit derived from road and roof surfaces during heavy rainfall. After grit separation and screening the sewage is subjected to sedimentation in which impurities in the form of suspended solids gradually settle and are removed in the form of a liquid sludge. Secondary treatment involves the use of biological filters in which bacteria, protozoa, fungi, worms, larvae and flies convert the impurities in the settled sewage. The final process involves a further settling or filtering referred to as 'polishing', before the final effluent is returned to the receiving watercourse.

ESSENTIAL PARAMETERS

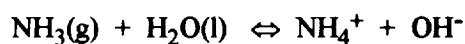
In order to monitor and control the entire process for the majority of the time, excluding accidents and emergencies, there are several parameters which can be used to give guidance on the state of the treated sewage. These include temperature, flowrate, dissolved oxygen content, pH, and turbidity. The quality of the final effluent depends upon its biological and chemical activity, and historically these are determined by the chemical and biological oxygen demand, however there are certain specific components which require more detailed measurement, and one of these is ammonia.

THE ROLE OF AMMONIA

Ammonia is present in natural body wastes and is formed by microbial action on the organic nitrogen containing chemical species present in the sewage. In the time it takes the sewage to reach the treatment works, virtually all of the nitrogenous species have been converted to ammonia. In addition the run-off from farmland introduces ammonia directly or more nitrogenous material to the watercourses. Ammonia levels are reduced in the sewage treatment process by 'nitrification', the process by which particular bacteria convert ammonia to nitrate in the presence of oxygen. Ammonia causes specific problems if the levels are too high in freshwater supplies. Firstly, it is toxic to fish. Fish kills are immediately obvious and prompt swift action by the public and the NRA. Secondly, ammonia prevents effective disinfection of water by chlorination, resulting in drinking water supplies with high bacteriological activity. If a Water Authority returns treated sewage with a high ammonia content to the river, kills a lot of fish, then abstracts the water downstream and fails to disinfect it effectively before supplying it as drinking water, the local populace tends to take a pretty dim view. The concentration of ammonia in water is therefore regarded as a critical parameter.

AMMONIA IN WATER

Ammonia in water is subject to an acid-base equilibrium:



for which $I: K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3]$

Since water is also ionized:



for which 2: $K_w = [\text{H}^+][\text{OH}^-]$

For simplicity all activity coefficients have been assumed to be unity.

Equations 1 and 2 can be combined to give:

$$3: \quad [\text{NH}_3] / [\text{NH}_4^+] = K_w / K_b [\text{H}^+]$$

from which 4: $\log [\text{NH}_3] / [\text{NH}_4^+] = \log K_w - \log K_b + \text{pH}$

The ratio of free to ionized ammonia is crucial, since it is neutral ammonia which is toxic to fish¹.

If virtually all the ammonia is present in the free form, i.e. at least 99%, then $\log [\text{NH}_3] / [\text{NH}_4^+]$ would be >2 . Since K_w is typically 3×10^{-15} and K_b is 1.6×10^{-5} then the pH would have to be at least 11.5. By adding KOH to the sample to raise the pH to at least this level, the total ammonia concentration in the sample can be determined. Knowing the original pH of the sample prior to the addition of KOH, allows the level of free ammonia in the sample to be calculated.

At the present time the total ammonia level is measured and the neutral ammonia calculated, with varying degrees of complexity, using the measured temperature, pH and a knowledge of the typical level of total dissolved solids in the sample. The accuracy of this method is limited primarily by the accuracy of pH measurement. Tables of data are available² which relate the percentage of unionized ammonia to pH, temperature and total dissolved solids, and also give the total ammonia concentration which would breach the EC directives for protection of fish stocks as a function of these variables. Table 1 gives a selection of percentages of unionized ammonia as a function of pH and temperature with a total dissolved solid level of 400mg/l, while Table 2 gives selected concentrations of total ammonia having a free ammonia level of 0.021mg/l (the current mandatory EC limit) as a function of pH and temperature for the same level of total dissolved solids.

Table 1: Percentage unionized ammonia as a function of pH and Temperature

pH	Temperature (°C)			
	5	15	25	35
5.5	0.0036	0.0078	0.0162	0.0321
6.5	0.0355	0.0778	0.1616	0.3196
7.5	0.3542	0.7727	1.5924	3.1063
8.5	3.4330	7.2250	13.928	24.276
9.5	26.226	43.781	61.806	76.224

Table 2: Concentration of Total Ammonia (mg/l) containing an unionized ammonia level of 0.021 mg/l as a function of pH and temperature with 400mg/l total dissolved solids.

pH	Temperature(°C)			
	5	15	25	35
5.5	579.1	264.4	127.2	64.24
6.5	57.93	26.46	12.74	6.443
7.5	5.812	2.664	1.293	0.663
8.5	0.600	0.285	0.148	0.085
9.5	0.079	0.047	0.033	0.027

REQUIREMENTS FOR AN AMMONIA ANALYZER

The majority of Ammonia analyzers currently use ion-specific electrodes with pH reference electrodes to perform the ammonia measurements. The typical life of electrodes in continuous operation is 3 months. The total ion measurement is performed by raising the pH using caustic solutions until virtually all of the ammonia is present in the unionized form. The ion-specific electrodes are subject to drift and therefore require calibration on a continuous basis. This type of analyzer is very expensive to maintain in terms of the cost of consumables, frequency of replacement and required routine maintenance. In addition the accuracy of the final result is subject to question.

Any replacement analyzer would need to demonstrate improved performance capabilities in terms of data reliability, while showing marked improvements in the cost and consumption of consumables, together with significant reductions in required maintenance. It would also need to be capable of long-term unattended operation with all data available for transmission to remote locations on demand.

THE NEED FOR SAMPLE PREPARATION

The initial stages of proof of the viability of a new analyzer involve demonstrable performance, under controlled conditions, using known solutions of ammonia in clean water, at different pH levels over a range of temperature. These initial studies assess accuracy, precision, stability, consumables and maintenance with a view to estimating the potential whole life costs of the analyzer.

Having successfully negotiated this phase of the evaluation, the next step is to undertake field trials. It is at this point that all previous problems pale into insignificance. The actual real world sample is an unstable liquid of unknown chemical and biological activity, containing a variety of suspended species. The presence or absence of light encourages bacterial growth as does temperature, and any surface acts as a growth medium. The only guarantee is that the major component will be water.

The analyzer is required to sample this liquid 24 hours per day for long periods without any maintenance and without any degradation of analyzer performance. In order to do this some form of continuous sample preparation is essential.

SAMPLE TREATMENT

The initial step is to transfer the sample to the analyzer. This has to be done on a continuous basis and, if a free ammonia measurement is being made, without changing the relevant conditions of the sample. This usually entails transfer at high velocity through smooth bore, light proof pipework using an appropriate long life pump.

In order to prevent degradation of the analyzer it is necessary to reduce the amount of suspended material and to prevent biofouling. Biofouling is caused by the initial coating of surfaces by active organic materials, followed by the use of these organics as a source of food by bacteria which subsequently multiply forming films of slime. As these films build up, the bacteria on the original surface wall are starved of dissolved oxygen in the liquid and die, causing sections of slime to detach from the walls and flow with the liquid. Biofouling can lead to the loss of ammonia by nitrification resulting in inaccuracies in the recorded measurements, and also to alteration of flowrates and blockages within small bore tubing in the analyzer. It is necessary to have a means of continuous filtration together with biocidal and algacidal treatment. All of these processes must be done on a continuous basis, involve minimal low cost consumables and operate for long periods without maintenance. In addition, none of these processes must affect the concentration of ammonia in the liquid, nor the ratio of free to ionized ammonia.

Ideally this whole treatment process is continuous and uninterrupted, so that sample is constantly available for transfer to the analyzer to determine the ammonia concentration.

FREE VERSUS TOTAL AMMONIA

On the assumption that an improved analyzer measures both free and total ammonia, rather than measuring one and calculating the other; then, provided the concentration of ammonia is effectively unchanged by the pre treatment process, and that the ratio of free to ionized ammonia is unaltered, a measurement of the free ammonia content may be made on the treated sample. In order to perform the total measurement, the pH of the sample must be increased so that all of the ionized ammonia is converted to free ammonia and the measurement repeated.

Table 3 lists some of the proposed Environmental Quality Standards for ammonia in water in connection with EC directives³, where * indicates mandatory limits.

Table 3 WRC recommended EQS values for Total and Unionised Ammonia.

Type	Usage	Total mg/l	Unionised mg/l
Fresh	Abstraction to Potable Supply		
	Treatment A1	0.04	
	A2	1.17*	
	A3	3.1*	
	EC designated Salmonid and Cyprinid waters	0.78*	0.021*
	Non-EC designated waters		0.015
	Industrial abstraction for Food Processing	0.04	
Salt	Protection of saltwater fish and shellfish		0.021

The required ranges for detection of total ammonia are 0 - 1 mg/l for drinking water treatment processes and 0 - 20 mg/l for sewage treatment processes². Recorded mean total ammonia levels in UK freshwaters vary from 0.007 to 8.2 mg/l¹. Published data indicate that in many other EC member States permitted levels are also exceeded. Similar trends are observed in EC tidal estuaries. Although considerable data are available there is not always corresponding information on the fishery status at these sites, and the effects of high ammonia levels on these ecosystems cannot be assessed.

Because of the conservative nature of the Water Industry, the fact that legislation currently requires the measurement of total ammonia, that the Industry has no experience of IMS as a measurement technique, and that Graseby is not known as a supplier to the Water Industry; it has been decided that the first monitor will be completely conventional and measure total ammonia. Once IMS, the technique and Graseby have been accepted, a free ammonia monitor can then be made available, since there are moves within the NRA and the WRC to change from measuring total ammonia to free ammonia.

IMS DETECTION OF AMMONIA

As everyone skilled in the art of IMS knows, ammonia is readily detectable, however there have always been problems associated with obtaining fast response and recovery characteristics. In addition the ammonia monitor for water is going to be sampling ammonia in liquid water and inevitably high humidity levels will be present. Although high humidity levels are normally regarded as anathema in IMS, they do assist in the desorption of ammonia from surfaces. A careful choice of dopant is required to eliminate interferences and give acceptable ammonia peak resolution and sensitivity, while having a high tolerance to humidity. Careful attention to the design of the detector front end, the choice of materials, the design of the water/air interface and the optimization of flow characteristics are all of vital importance in achieving the required performance characteristics combined with stability and long life.

PERFORMANCE

When we embarked on this project and did a preliminary assessment, we set ourselves a design goal of 6 months for operating periods between maintenance for the complete system, based on what we thought could be achieved realistically with an IMS system and what we assumed a bought in pre treatment system would deliver. When we spoke to the WRC and to manufacturers of Ammonia Analyzers and Filter Systems, the scheduled maintenance for Analyzers ranged from twice daily to two to three weeks at best, while that for Filter Systems ranged from a few days to a maximum of one month. All of the required maintenance activities and costs were significant, involving expensive consumables such as chemicals and filters. The reaction to our proposed design goal was one of incredulity. Our first experience of a bought-in Filter System enabled us to understand this attitude.

The manufacturer had tailored the system to our requirements and recommended that we use a cross-flow filter system with a compressed air backflush facility. Two filters were incorporated, one active and one in standby mode. A daily backflush cycle had been recommended. After installation at our test site and extensive modification resulting in the backflush cycle being carried out every three minutes, the longest period of continuous operation achieved was 2 days. At the end of this period the entire filter system had to be stripped down and manually cleaned.

At the present time after extensive laboratory testing of the analyzer, and approaching a year of field testing for the analyzer and pre treatment system, we believe that the 6 months maintenance cycle for the analyzer is achievable, while that for the pre treatment system is currently being pushed towards this figure.

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