Sampling in combination with process knowledge as critical factors for the reliability and accuracy of laboratory testing

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Eurachem workshop 2023, Bern, Switzerland
22 – 23 May 2023

INTRODUCTION

In today's highly complex and demanding market of analytical services, it is of outmost importance that laboratories safeguard the reliability and accuracy of their results. Amongst many other important factors, our experience during the last three decades has demonstrated that a carefully planned sampling protocol is not by itself adequate in satisfying above requirement. It shall always be born in mind that making correct sampling decisions necessitates good knowledge of the actual process that is being monitored.
Selected cases from our involvement in the commissioning and subsequent operation of large-scale projects (e.g. Seawater Reverse Osmosis Plants - SWRO's, sewage treatment plants and renal wards in healthcare establishments), will be presented. These will provide well justified real-life examples of how critical can process knowledge be in the design and monitoring of sampling activities. Particular reference will be made to the impact on the reliability and also interpretability of test results.

METHODOLOGY

The size and complexity of a small market in which we have been operating during the last 33 years, dictates a flexible approach to dealing with customer enquiries. This applies to both routine and regulatory compliance testing and also to forensic-type investigations. In this context, the lab engages in several sampling activities in order to obtain first-hand evidence and justification as a means of being able to provide reliable, accurate and interpretable results to the customer. This becomes especially useful in the context of our accreditation in the expression of O & I's.

The following cases will be cited as typical examples of how process knowledge optimises the sampling protocol and the subsequent interpretation of results.

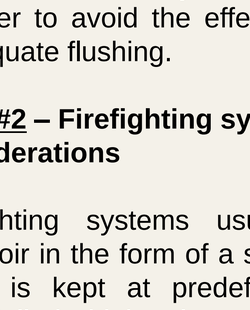
CASES

Case #1 – Residual biocide measurements following cleaning and disinfection activities

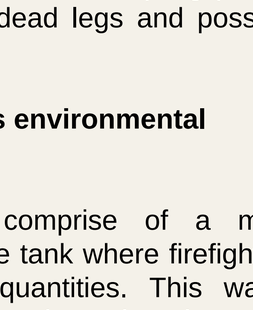
Severe fluctuations in the mains water quality of the island during the past three decades, pose demanding requirements in monitoring of hot and cold water systems, including cleaning and disinfection.
Our lab is often called to assess the effectiveness of such activities. This involves site visits during which sampling takes place. Sampling however, needs to be carefully targeted in order to provide objective data about the results of the maintenance activities. This necessitates carefully deciding on the sampling points, in order to avoid the effect of dead legs and possibly inadequate flushing.

Case #2 – Firefighting systems environmental considerations

Firefighting systems usually comprise of a main reservoir in the form of a storage tank where firefighting water is kept at predefined quantities. This water, especially in high-volume systems (e.g. shopping malls and office complexes) needs to be carefully maintained and preserved, as prolonged stagnancy can create serious biofouling and corrosion problems which may impair the performance of the system in real life scenaria. For this reason, and in the context of proactive system maintenance, several chemicals are added into the water as, for example corrosion and scale inhibitors. Apart from the need to monitor the concentrations of these chemicals at prescribed intervals, it is also equally important to replenish these chemicals as and when required (i.e. during leakages and when there is a need to get rid of old and/or stagnating water and top-up with fresh water). During these maintenance activities, special environmental considerations apply, as any rejected water needs to comply with the provisions of disposal permits issued by the local environmental authorities.



Typical firefighting system installations



Typical sampling point

In the context of this case study, a specific disposal permit needed to be considered in order to decide where the water was to be disposed off. There was a choice of a nearby water receptor (rainwater reservoir) or direct disposal into the domestic sewage collection system. In these cases, nitrite concentration (a widely-used corrosion inhibitor) must be strictly monitored as this is highly toxic to humans and aquatic life.
Our lab was provided with an initial set of data showing the results from two sampling points within the firefighting system and the corresponding disposal permit limits. These are shown in table 1.

Table 1: Initial data provided by customer

Determinant	Unit	Sampling point #1	Sampling point #2	Disposal permit limits
TN	mg/L	11,2	11,9	15
Nitrites	mg/L	17,8	1,09	-
TOC	mg/L	12,3	-	-

Our experience in similar projects dictated that above results needed verification and maybe additional sampling, simply because typical nitrites concentrations in closed systems range at concentrations of up to two orders of magnitude higher. Therefore, we recommended visiting the site and sampling from targeted points in the whole loop.
During the site visit, and on the basis of additional information, it was suspected that several dead legs might not be considered in the results provided by the customer and, with this in mind, additional samples were taken.
The results are shown in Table 2.

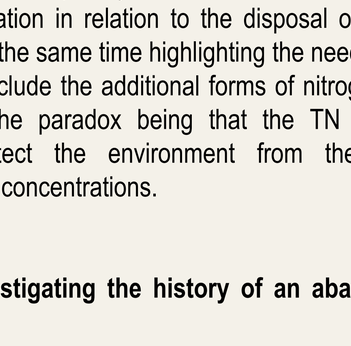
Table 2: Additional data after site visit

Determinant	Unit	Sample A	Sample B	Sample C	Sample D	Sample E	Disposal permit limits
TN	mg/L	7,3	6,0	464	8,8	6,3	15
Nitrites	mg/L	0,489	0,019	1195	9,87	0,087	-
TOC	mg/L	1,826	2,578	24,13	121,7	8,56	-

Above results basically provided a totally different picture, verifying our initial suspicion and also severe fluctuations in nitrite concentration. Consequently, this dictated the need for a very careful consideration in relation to the disposal of water from the system, while at the same time highlighting the need for the disposal permit to also include the additional forms of nitrogen and not only total nitrogen; the paradox being that the TN alone does not adequately protect the environment from the corresponding equivalent nitrite concentrations.

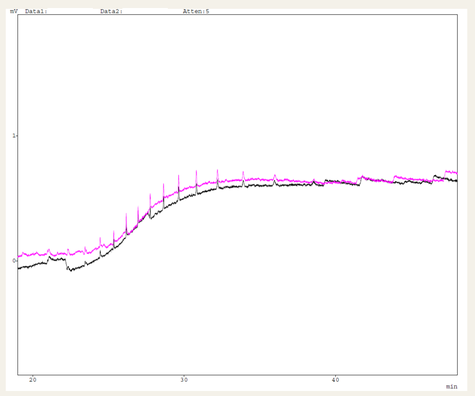
Case #3 – Investigating the history of an abandoned subsea pipeline

Unusual subsea findings attract a lot of attention, especially in the context of environmental awareness. One such case was encountered during a coastline survey which was part of the baseline environmental study of a seaside project.
An abandoned subsea pipeline was discovered and the contractor was asked by the local environmental authority to investigate its nature. The enquiry came to our lab with additional information that other similar pipelines were found in the area and which were known to be related with the uploading of fuel for the nearby industrial area. Further historical investigation revealed information about the actual type of fuel that was used by the local industry. We therefore recommended that samples were taken from both pipelines, with the aim to attempt a comparison of the two types of residues within the pipes.

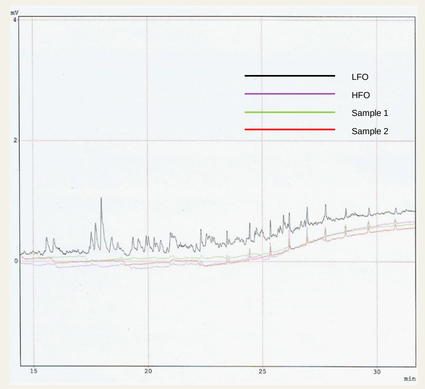


Residue samples from within pipelines 1 and 2

Qualitative chromatographic investigation verified a very high degree of correlation between the two chromatographic profiles. This was basically verifying that the unknown pipeline was also, most possibly, carrying the same type of fuel.
The comparative chromatograph is shown below.



Furthermore, an attempt was made to verify the historically proven information that the fuel uploaded through the known pipelines was a combination of HFO and LFO. This additional investigation showed a high degree of correlation between the two samples and the heavier fractions of LFO and HFO, while at the same time clearly demonstrating the weathering effect on the light LFO fractions in the two samples.



Case #4 – Verifying the possible source of an illegal dumping incident into domestic sewage collection systems

One of the major STP's of the island was suspecting possible dumping of waste from a dairy industry in the nearby community. There was organoleptic evidence from the plant operators supported by additional analytical data produced by the plant's in-house lab (e.g. elevated COD results).
An initial 24-hour composite sample was delivered to the lab and the results were inconclusive, so we recommended taking additional targeted grab samples, that would be expected to provide enhanced evidence of this on the basis of carefully selected parameters.

The following results were obtained:

Parameter	Unit	Composite sample	Grab sample A	Grab sample B	Grab sample C
pH	-	7,29	6,11	5,31	6,62
Electrical conductivity	mS/cm	1,734	2,533	2,576	2,160
Chlorides	mg/L	304	536	417	511
BOD	mg/L	434	1604	1671	936
COD	mg/L	900	2940	2844	2094
Calcium (aqua-regia digestion)	mg/L	44,4	70,5	93	102
Phosphate Phosphorus	mg/L	5,12	14,54	17,52	19,18
NH_4-N	mg/L	60,3	80,1	61,4	62,4
Total Nitrogen (TN)	mg/L	84,2	139,7	119,4	115,9
Total Phosphorus (TP)	mg/L	11,13	25,13	22,00	20,38

The composite sample shows limited evidence to support their suspicion (reduced pH and slightly elevated TP). However, the grab samples clearly confirmed the dairy origin of the waste, as exemplified by the typical footprint of dairy waste composition.

ACKNOWLEDGMENTS

We express our thanks to all members of staff who have been contributing to the collection of valuable laboratory data and information during the past three decades in the context of their daily activities.

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