

Industrial Process–Wastewater Analysis by CLADE™ MIRA Analyzer

Water quality is increasingly becoming an important issue for industry, the environment and our daily lives.[1] In many cases, the treatment of industrial process wastewater requires complex analyses, often lasting several hours or even days.

The CLADE™ MIRA Analyzer not only enables direct analysis by production teams but also swiftly generates results within 4 minutes.

Scope

In this study, samples from an industrial process-wastewater containing four analytical targets were investigated using the CLADE™ MIRA Analyzer. The wastewater stream contains organic materials, salts, and an acid. The pH of the wastewater typically falls within the range of 4.0 to 4.8.

Table 1 summarizes the ingredients as well as the expected concentration range for each substance in the stream, as provided by the customer in the first column.

	Expected concentration[g/L]	Concentration for Model Calibration [g/L]	RMSECV [g/L]	RMSEP [g/L]
Acetic acid	5 – 10	4 – 11	0.03	0.06
Ammonium chloride	0.05 – 0.20	0 – 0.22	<0.01	0.02
Propanol	1 – 3	0.75 – 3.25	0.03	0.05
NaCl	12 – 20	10 – 22	0.11	0.15

Table 1: Components within the wastewater stream and their expected concentration range, as well the concentrations used for training and validating the models. Model performance values are also provided for each compound.

The CLADE™ MIRA Analyzer grants quantitative results for all analytes within 4 minutes without the need for sample preparation. This guarantees fast processing of the wastewater to the purification plant, minimizing the need for storage tanks.

If the wastewater contains substances outside the defined concentration range, or contaminants, it will be considered off-spec.

The focus of this application note will be on ammonium chloride, which has the lowest concentration among the ingredients, but is known to have adverse environmental impacts.[2] This aspect makes an estimation of the limit of detection (LOD), and limit of quantification (LOQ) relevant for ammonium chloride.

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Methods and Results

Based on the design of experiment (DoE) principles, 19 training samples were prepared with a design resolution of 5. As shown in Table 1, the concentration range of the training samples exceeds that of the wastewater process, to ensure the robustness of the results in the operational window of the process.

Sample spectra were measured with three-fold repetition, exhibiting a high repeatability with a standard deviation of only 0.07 %. This is a strong indicator for the high robustness of the measurements. The spectra and their corresponding concentrations were used to train partial-least-square regression (PLS) models for each ingredient. The error for training the data is presented in Table 1 using root-mean-square error of cross-validation (RMSECV, leave-one-out method).

LOD and LOQ were calculated for ammonium chloride based on the PLS model, resulting in a concentration of <0.01 g/L and 0.02 g/L, respectively.[3] These values are significantly lower than the interval defined for the concentration of ammonium chloride within the wastewater process, promising a high sensitivity of the analysis.

PLS score distances as well as orthogonal distances were used to define the threshold of the calibration coordinates, which is beneficial for the detection of outliers.

Ten samples were prepared for validation of the models' performance. Two of the validation samples included off-spec features, namely higher-than-expected ammonium chloride concentration (1.12 g/L in sample "Val_01") and a contaminant salt (3 g/L sodium sulfate in sample "Val_02"). The overall performance of each model for predicting the validation samples is exhibited in Table 1 using root-mean-square error of prediction (RMSEP).

Here, the focus will be on presenting the validation results for ammonium chloride. Figure 1 shows the high correlation between ammonium chloride's spectrum in water with the regression coefficients emanating from the PLS model. This promises the effectiveness of the model in quantifying the compounds and its robustness against matrix influences. The number of latent variables is chosen based on the minimization of the cross-validation error.

Figure 2: Predicted concentrations vs. actual concentrations for ammonium chloride, using validation samples. Samples marked in red are identified as outliers.

Outlier detection is based on a data-driven approach with an outlier significance level of $\gamma = 0.01$ and extreme significance level of $\alpha = 0.05$.^[3] Figure 3 shows the normalized orthogonal distance (Q-res) vs. PLS score distance (Hotelling's T2 values) for PLS decomposition of the validation spectra. The results are presented for the case of ammonium chloride. Red-marked samples are identified as outliers.

The spectra recorded from sample Val_01 could be transformed by the PLS model with small changes (low orthogonal distance) but the sample is far from the coordinates of the calibration samples (high score distance). Val_02, on the other hand, shows high distance in both axes, mainly due to the presence of a contaminant, for which the PLS model is not trained.

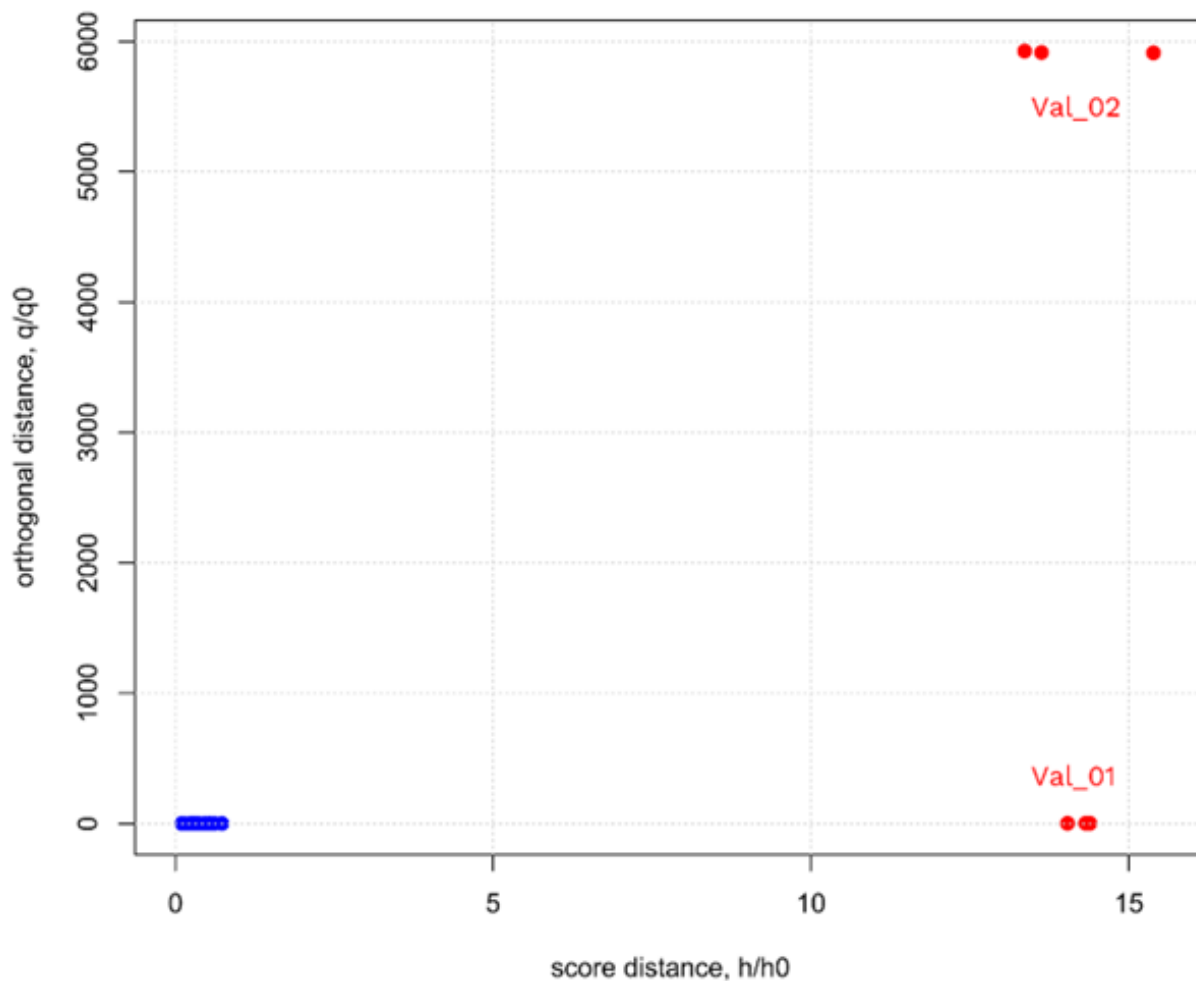


Figure 3: Orthogonal distance vs. PLS score distance for ammonium chloride, using validation samples. Samples marked in red are identified as outliers.

Summary

The CLADE™ MIRA Analyzer was able to robustly measure the concentration of the ingredients in an industrial wastewater stream in 4 minutes.

Samples needed no extra preparation and were taken directly for analysis.

Error of the analysis as well as the LOD and LOQ were significantly smaller than the specified interval for the given process parameter, as defined by the customer. This is evidence for a high sensitivity of the method.

IR spectrum of ammonium chloride correlated with the regression coefficients obtained from the PLS model. This indicates the effectiveness of the model in quantifying the compounds and its robustness against matrix influences.

The analytical method was able to detect outliers that contained out-of-bound ammonium chloride or contaminants (sodium sulfate).

References:

[1] <https://www.eea.europa.eu/ims/industrial-pollutant-releases-to-water>

[2] <https://pubchem.ncbi.nlm.nih.gov/compound/Ammonium-Chloride#datasheet=LCSS§ion=InChI>

[3] F. Allegrini and A. C. Olivieri, *Anal. Chem.* 2014, 86, 15, 7858–7866, <https://doi.org/10.1021/ac501786u>

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