

# Surface waters: Measuring background levels of free cyanide

Free cyanide is highly toxic towards aquatic organisms. Environmental quality standards for free cyanide were recently proposed under the European Water Framework Directive. However, current detection methods are not sensitive enough to measure the proposed levels accurately. Fraunhofer IME researchers have adapted an existing analytical method for free cyanide and investigated background concentrations in surface waters to facilitate compliance testing.

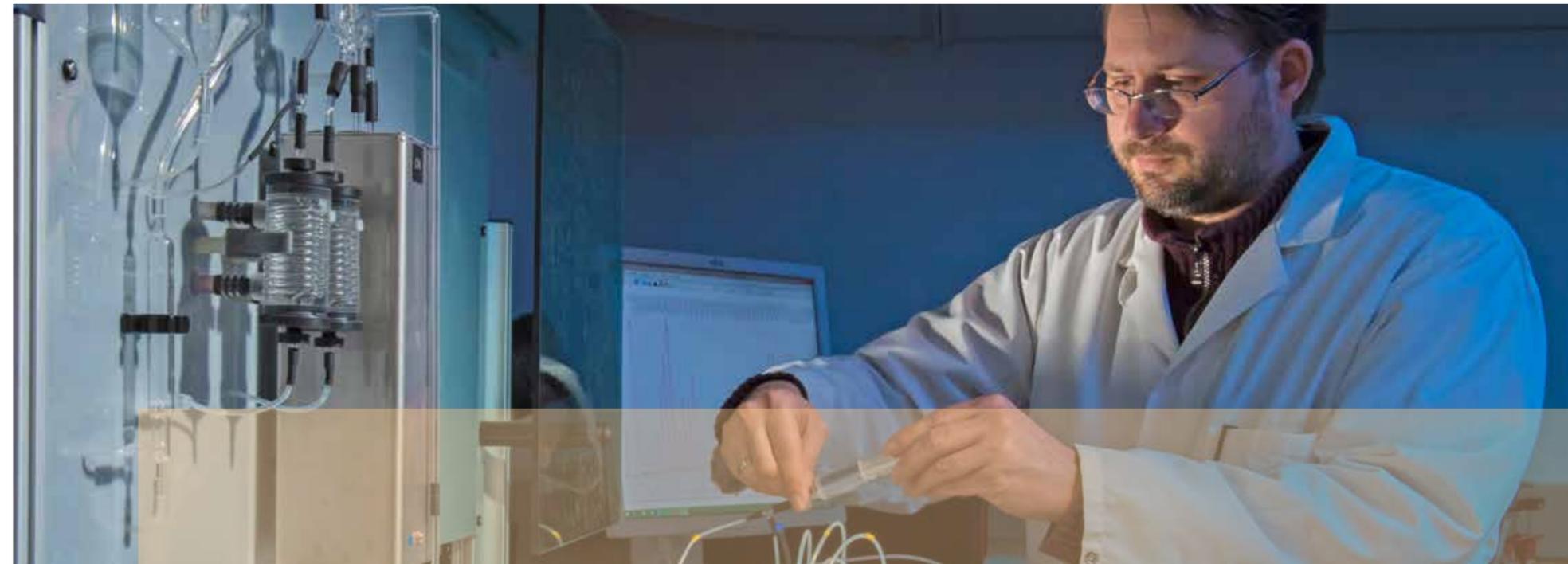
Cyanide is a naturally occurring compound which is cycled in the environment by cyanide degrading organisms and those which assimilate cyanide. Natural background concentrations of cyanide can originate from the degradation of plants and microbes such as algae. For cyanide in waters, a distinction is made between “total cyanides”, defined as all simple cyanide compounds and complex structures containing cyanide, and “easily liberated / weak and dissociable cyanides”, comprising hydrogen cyanide and all compounds that release hydrogen cyanide at pH ~4. The latter is the highly toxic “free cyanide”.

“We currently lack reliable data on the background concentrations of free cyanide in surface waters,” says project coordinator Burkhard Knopf. “However, the scientific literature indicates that background levels derived from plant and microbial processes should be half a microgram to ten micrograms per liter.” Recently, the UK Environmental Protection Agency proposed an environmental quality standard (EQS) of 0.26 µg/L free cyanide under the Water Framework Directive,

to avoid long-term adverse effects in freshwater systems. The European Union Joint Research Centre (JRC) has proposed an annual average EQS of 0.5 µg/L free cyanide. The Water Framework Directive mandates that analytical methods used to determine compliance with EQS levels must have a limit of quantification (LOQ), defined as the quantity of analyte in a sample that can be measured reliably, of at least 30% of the EQS concentration. “But current methods for the measurement of free cyanide in waters only

achieve LOQs of approximately one microgram per liter, so more sensitive methods are required,” explains Knopf. “A consortium of industry associations therefore initiated an investigation by Fraunhofer IME to implement and test a fit-for-purpose method that provides reliable data for free cyanide background concentrations in surface waters.”

As method Knopf and his team selected continuous flow analysis where samples are directly injected into a constant flow of reagents and are transported, after different chemical reactions in the system, to the detector.



## The selected method was implemented and validated according to ISO 17025 accreditation requirements

Free forms of cyanide occur naturally in the environment and are highly toxic. Cyanide levels are influenced by a combination of different parameters.

This approach was selected because the technical requirements are ideal for the optimization of sensitivity. Photometric detection is needed to

detect low concentrations of cyanide, so the IME researchers selected a continuous flow photometric analysis system with a special cuvette installation. The target LOQ

was approximately 30% of the proposed EQS concentration (i.e. ~0.15 µg/L) to ensure compliance testing with the proposed JRC EQS concentration of 0.5 µg/L. Knopf: “We determined the LOQ and the limit of detection, in short LOD, the latter defined as the concentration at which an analyte can be qualitatively detected in a sample, in two separate measurement series at a 95%

confidence level according to the German standard DIN 32645.” Under optimal test conditions the LODs were below 0.04 µg/L and the LOQs were below 0.14 µg/L. The researchers predict that routine test conditions should achieve LOQs about 0.3 µg/L. During the validation process, the analytical precision, selectivity, robustness and measurement uncertainty of the improved method were found to be sufficient. However, the investigations of Knopf and his team showed that all reagent solutions have to be free of any gas to reduce disturbances of the measurements by interfering influences and the used reagent solutions have to be prepared freshly.

“We carried out tests to confirm that the improved method was suitable for testing field samples and also investigated whether samples can be

The Water Framework Directive of the EU aims at assuring a good status of all water bodies – toxic compounds have to be tested for exceeding potential effect levels



To measure concentrations of cyanide, researchers took water samples from different positions along the course of the River Lenne and stabilized them before transfer to the laboratory.



Dr. Burkhard Knopf: "Previous techniques for measuring free cyanide in lakes and rivers achieved a limit of quantification of approximately one microgram per liter. Our modification of an existing method now achieves measurements of far greater sensitivity."

### The suitability of the improved protocol for the measurement of free cyanide was demonstrated using field samples

stabilized for at least 24 hours before testing. In February and March 2016, we therefore collected several sets of samples from along the River

Lenne near Schmalenberg for analysis according to Water Framework Directive requirements," says Burkhard Knopf.

Samples were collected from the river's spring and from downstream locations. For transport and storage, the samples were stabilized by adjusting to pH 12 and keeping them in the dark at 4°C. Lenne water samples spiked with cyanide standard were used as positive controls. This approach was sufficient to stabilize the samples and the field validation results were satisfactory, confirming that the protocol is fit for purpose.

Analysis of the samples from the River Lenne confirmed the expected low levels of free cyanide

in natural waters, with mean concentrations from both sampling campaigns in the range of the LODs (up to 0.36 µg/L). There were significant differences in free cyanide concentrations between the spring, with levels mostly below the LODs, and four downstream sampling points, with free cyanide concentrations at least 50% higher, possibly due to degraded plant biomass in the water.

The concentration of free cyanide can be influenced by physicochemical parameters such as pH, oxygen concentration, conductivity, non-purgeable organic carbon, metals, and water hardness. Surface water samples were therefore taken at four different locations differentiated by parameters such as the level of solar radiation and water velocity. In one campaign, samples were also taken at different times of day. The Fraunhofer IME team chose sampling sites at the River Lenne and the Esmecke Barrier Lake.

### Background levels of free cyanide in uncontaminated surface waters were below the proposed environmental quality standard of half a microgram per liter

Free cyanide concentrations were generally low, ranging from below the LOQ to ~0.24 µg/L. There were significant differences between stagnant and flowing water, with concentrations of free cyanide at the river sites 23–30% lower than the cyanide levels in the lake. The lake and river samples also differed in terms of their copper, sulfur, phosphorus and potassium concentrations, which were higher in river water, whereas non-purgeable organic carbon concentrations were higher in the lake. The stagnant water samples had consistently lower oxygen concentrations and were more acidic. The time of day had no significant impact on free cyanide levels. There does not appear to be a single major parameter that influences free cyanide concentrations in surface waters. The cyanide levels were influenced by combinations of parameters, although it is important to note that the overall differences between cyanide concentrations were small.

"Our investigation showed that background concentrations of free cyanide in the waters we tested were below the EQS of half a microgram per liter

proposed by the JRC. However, the analysis of further river and lake waters from different geographical regions is necessary to create a reliable database and to identify possible influencing factors," says Burkhard Knopf.

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