

METHOD DEVELOPMENT OF A SEGMENTED FLOW SYSTEM FOR THE ANALYSIS OF TOTAL CYANIDE IN DRINKING WATER AND NATURAL WATERS USING AN ON-LINE UV DIGESTION AND AMPEROMETRIC DETECTION



Drinking water regulations are quite extensive and complex. In terms of water quality, the water supplied to customers must meet a set of very high standards, mostly health-based but also with a view to assure the high quality of drinking water long term. Wholesome water as defined in the regulations, must meet all the chemical, physical and bacteriological high standards as stipulated in the legislation, and must also be perceived by the customers to be of high quality. The analysis of total cyanide in drinking water is required under The Water Supply (Water Quality) Regulations within the chemical parameters schedule. Total cyanide in drinking water should not exceed the value of 50 ug/L, its prescribed concentration or value at the point of compliance, i.e., the consumer's tap. This is a conservative value, as it is much lower than the short-term exposure health-based value estimated by the World Health Organisation, WHO. This is because cyanide is a parameter of high acute toxicity.

The limit of quantification - LoQ and ongoing performance criteria is also stipulated in the water quality regulations. In the case of total cyanide this requires a maximum LoQ of 15 ug/L and a maximum estimated uncertainty of measurement of 30% at the PCV level. This requires techniques that are not only sensitive, but reproducible and accurate, and critically also robust, for example that can operate with a consistent response for long runs and that can cope with various matrix types.

Due to its reactivity, cyanide ion presents in water typically combined with other chemical forms, for example in metal complexes. These complexes vary in strength, and this influences how stable they are in water. Some complexes are easily dissociable and break down in the presence of acid, e.g., KCN, and others will have increasing strong metal-cyano bonds that require more aggressive approaches, like those of Iron. The toxicity is associated with the cyanide ion, so the analytical



The Systea® analyser system at affinity Water Laboratory

technique must be capable of effectively extracting the cyanide ion from these complexed species, so it can be accurately measured. A digestion step in the analysis is required to achieve this. All these chemical species containing the CN⁻ ion, will form the total cyanide.

To maintain sample integrity through transport and storage, samples for this analysis must be preserved upon collection with a dechlorinating agent, to prevent the total cyanide from being lost as free cyanide, a readily volatile species. Further preservation is also required with Sodium hydroxide to ensure that any cyanide or cyanide species present are kept in ionic form.

Affinity Water labs has selected a Systea® analyser for this compliance analysis. The principle of operation is based on the reference method ASTM D7511-09E2 for the analysis of total cyanide by segmented flow injection with in-line UV digestion module and amperometric detection. The digestion is achieved

under the action of UV light. This breaks down the complex cyanides into CN⁻ ion, which is captured in a basic acceptor solution. After digestion, the flow is then acidified and the resultant HCN passes through a gas diffusion membrane onto a carrier solution for detection using a silver electrode.

Dechlorinating agents typically used for total cyanide are ascorbic acid or sodium thiosulphate. The first option can lead to false positives in waters disinfected using chloramination, and the latter can interact with the silver electrode used for the detection, creating a positive bias. The method development in the Affinity Water laboratory focused on creating a laboratory method that allowed for the use of thiosulphate as the dechlorinating agent of choice, which was successfully achieved. The method has a working range of 0-20 ug/L, and a limit of quantification 2.8 ug/L. The method has been validated and it's awaiting accreditation under ISO 17025-DWTS.

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