



Extramural Research

Final Report: Low-Level Speciation of Cyanide in Waters

EPA Contract Number: 68D01023

Title: Low-Level Speciation of Cyanide in Waters

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Phase: I

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Project Amount: \$70,000

RFA: Small Business Innovation Research (SBIR) - Phase I (2001)

Research Category: [Ecological Indicators/Assessment/Restoration](#), [SBIR - Monitoring](#)

Project Research Results

- [Original Abstract](#)
- [2 publications for this project](#)

Grantee Research Project Results

[NCER Grantee Research Project Results](#)

Description:

Cyanide is generated by several major industries (e.g., power plants, aluminum production, and petroleum refineries) as a byproduct of their production processes, and also is used in large quantities for technical purposes in other industrial operations (e.g., gold/silver mining, base metal ore flotation, steel manufacturing, electroplating, and production of photographic materials). Due to its high (eco)toxicological potential, cyanide may lead to regulatory issues and environmental concerns. The actual chemical form ("speciation") in which cyanide is present is crucial for both the performance of technical processes in which it is used as well as for risk assessment of discharges. Consequently, methods for the determination of cyanide speciation are needed for proper investigation. Unfortunately, existing methods, especially those approved by regulators, only measure "total" cyanide, or the sum of the labile cyanide species commonly known as "WAD" (weak acid-dissociable) cyanide. This leads to an overestimation of the (eco)toxicological threat and prevents detailed knowledge of the fate of cyanide in technical processes, including waste treatment streams. Current U.S. water quality criteria for cyanide are set at $200 \mu\text{g L}^{-1}$ for drinking water for human consumption, and at $5.2 \mu\text{g L}^{-1}$ or $1 \mu\text{g L}^{-1}$ for the protection of sensitive wildlife in freshwater or seawater, respectively. These criteria are expressed as "free" cyanide, but currently available analytical methods cannot measure CN^- specifically and independent of all other cyanide species. Regulators tend to adopt these values for groundwater criteria and industrial discharge permits, but instead of using a common standard-define them as either "free," "WAD," or "total" cyanide. Additionally, EPA-approved methods for the determination of WAD cyanide (and total cyanide) typically are not sensitive enough in routine operation to yield reliable analytical results in the low $\mu\text{g L}^{-1}$ concentration range. Consequently, industries frequently find themselves in situations where regulations require them to achieve cyanide discharge concentrations at levels that cannot be measured reliably.

Consequently, this project is aimed at developing an analytical method that is capable of differentiating and positively quantifying all relevant individual cyanide species encountered in environmental and industrial waters, as well as in impacted soils, sediments, and solid wastes. Contrary to methods currently approved by regulating bodies, this will provide a detailed breakdown and exact characterization of total cyanide concentrations by combining a liquid chromatography-based separation with sensitive and cyanide-specific detection. In comparison to other previously published cyanide speciation techniques, this method incorporates all different types of relevant cyanide species (free CN^- , various metal-cyano complexes, and the nonmetallic species OCN^- and SCN^-). Currently, this method achieves detection limits between 0.5 and $2.5 \mu\text{g L}^{-1}$, which is at least one order of magnitude below those of other published methods. A novel wet-chemical reaction scheme for the conversion of cyanide species to free cyanide was developed, and membrane diffusion with amperometric detection was introduced as a detector for the separated cyanide species.

Summary/Accomplishments (Outputs/Outcomes):

In this project, Frontier Geosciences, Inc. (Frontier) developed a prototype analytical method for the separation and determination of several relevant forms of cyanide ("species") in waters by ion chromatography-anion self-regenerating suppression-conductivity detection-flow injection-gas diffusion-amperometric detection (IC-ASRS-CD-FIGDAD). The cyanide species are separated by anion-exchange chromatography using a hydroxide eluant. After the separation, the hydroxide eluant is neutralized by the self-regenerating suppressor before OCN^- is determined by CD. After this nondestructive detector, the chromatographic effluent enters the wet-chemical online reaction step, in which the other cyanide species are converted to free cyanide by acidic reductive ultraviolet (UV) photo-oxidation, before the evolved cyanide is separated from the liquid stream by gas diffusion across a membrane and measured by amperometric detection. At this point, the method yields detection limits of 0.5 - $2.5 \mu\text{g L}^{-1}$ (as cyanide) for CN^- , OCN^- , SCN^- , $[\text{Fe}(\text{CN})_6]^{3-}$, and $[\text{Co}(\text{CN})_6]^{3-}$.

The chromatographic separation between individual cyanide species as well as from known interferents, especially sulfide, was optimized. Frontier was unable to achieve intact elution of four other cyanide species: $([\text{Hg}(\text{CN})_4]^{2-})$, $([\text{Ni}(\text{CN})_4]^{2-})$, $([\text{Fe}(\text{CN})_6]^{3-})$, and $([\text{Au}(\text{CN})_2]^-)$, which appeared to be due to the decomposition of these complexes during separation and/or irreversible binding to the column material. Attempts to resolve these issues by using different stationary and mobile phases in anion-exchange chromatography, or by using ion-pairing chromatography as a separation mode, were unsuccessful. Near-quantitative and equal wet-chemical conversion of cyanide species to free cyanide were achieved by a solution of monopersulfate in hypophosphorous acid under UV irradiation for all nine species, except OCN^- and $[\text{Co}(\text{CN})_6]^{3-}$. Ligand competition was found to be ineffective for releasing cyanide from cyanide species, or produced unacceptable background signals from ligand decomposition products. The method validation study yielded very low detection limits for all separated cyanide species, and showed good reproducibility for standard solutions and for real-world samples.

An interference study was conducted for the known detection interferent sulfide, but no effects prohibiting quantification for any cyanide species were found up to sulfide concentrations of $\mu\text{g L}^{-1}$. Retention time shifts were observed for CN^- , and the sulfide peak overlaps partially with the cyanide peak at high sulfide/cyanide ratios. However, both effects do not impair cyanide quantification if its identification can be verified. Matrix spikes performed on complex real-world samples showed evidence of species conversion, and thus yielded low recoveries for the less-stable cyanide species (e.g., CN^-), while stable species such as $[\text{Co}(\text{CN})_6]^{3-}$, were recovered quantitatively. In mining process and discharge waters, CN^- , SCN^- , and $[\text{Fe}(\text{CN})_6]^{4-}$ were identified as the major cyanide species, and a number of unidentified species also were encountered. The agreement between the sum of the cyanide species determined by IC-ASRS-CD-FIGDAD and independently measured total or WAD cyanide concentrations were satisfactory for a prototype method, but indicated the need for further studies. Quantitative disagreement was at least partially due to interferences observed for the WAD and total cyanide determinations.

Conclusions:

In its present state, the method provides several advantages over other currently available analytical methods for cyanide determination and speciation. It is one of the first methods that can actually measure free cyanide (CN^-) independent of other cyanide species present with detection limits that allow for the analysis of anticipated environmental

concentrations. It is possible, however, that weak metal-cyano complexes in real-world samples would contribute to the free cyanide signal by decomposition during the current chromatographic separation. This would make the "free cyanide" result more comparable to "weak acid-dissociable" cyanide concentrations measured by EPA Method 1677. Contrary to most other previously published liquid chromatography-based cyanide speciation methods, which only measure a suite of different metal-cyano complexes, this approach also is capable of determining all relevant nonmetal cyanide species, namely free cyanide, cyanate, and thiocyanate. The selected detection approach is more sensitive and selective than any other technique previously used for the detection of cyanide species after separation. In future work, the chromatographic separation of cyanide species needs to be investigated in more detail to incorporate a number of additional metal-cyano complexes. Also, the current wet chemical reaction process must be expanded to provide quantitative conversion of very stable cyanide species such as OCN^- and $[\text{Co}(\text{CN})_6]^{3-}$.

After the termination of this Phase I project, the prototype method will be introduced to the market for routine analyses. After further refinement and improvement, Frontier anticipates having a fully developed and tested method available by January 2003. The new cyanide speciation capability will be available for monitoring purposes, as well as for the investigation of industrial and environmental cyanide issues in more complex research projects. After seeking approval of the developed method by regulatory bodies and/or organizations promoting standardized analytical techniques, the technology will be made available for transfer to other users, either directly from Frontier or via an instrument manufacturer as a commercially available instrument.

There are two major fields of application for the developed cyanide speciation method by IC-ASRS-CD-FIGDAD: the optimization of metallurgical processes and the design of treatment strategies that minimize cyanide discharges to the environment. Two major metallurgical processes employ cyanide. In gold and silver mining, cyanide is used in heap-leaching processes to extract the noble metal from the ore. For some base metal (e.g., Zn, Cu, Pb, Ni, and Co) ore flotation processes, cyanide is used to separate the desired ore (e.g., ZnS) from unwanted accompanying major minerals (e.g., FeS). Cyanide is a very expensive reagent, and much of the cyanide used in these metallurgical processes goes to waste because it undergoes unwanted side reactions that generate cyanide species other than those desired in the particular application. Consequently, the ability to distinguish between all possible different cyanide species in the metallurgical process could be used to optimize the process design and to minimize cyanide use, thus increasing the operation's profitability.

The described metallurgical benefits also entail positive environmental consequences, because a reduction of cyanide use in the mining operation often will simultaneously reduce cyanide discharge to the environment. This would, in turn, minimize the environmental impact of the mining operation, and thus reduce the cost of remediation measures and environmental liability. Along the same lines, the analytical capability also would be a very useful tool in the design of custom-tailored treatment strategies for reducing cyanide discharge, which could address the specific cyanide speciation distribution present. The benefit of optimizing the design of treatment technologies lies in minimized cost and maximized efficiency and success, as well as in the chance to adapt treatment technologies to each individual or changing situation based on the available speciation information. Finally, the developed method would be a valuable tool for risk assessment and (eco)toxicological evaluation of ongoing or historic cyanide discharges, because only free cyanide (CN-) is assumed to be highly toxic, and the toxicity of all other cyanide species is assumed to be based on the degree of their breakdown to free cyanide. The generated cyanide speciation data would provide the appropriate scientific base for discussions between dischargers and regulators with respect to discharge permits and cleanup goals. This could lead to accelerated agreement on economically feasible and protective regulations, and thereby improve the public perception of the dischargers.

Journal Articles:

No journal articles submitted with this report: [View all 2 publications for this project](#)

Supplemental Keywords:

gold mining, silver mining, base metal ore flotation, petroleum refineries, manufactured gas plants, aluminum refining, steel hardening, cyanide speciation, free cyanide., RFA, Scientific Discipline, Toxics, Waste, Water, Ecosystem Protection/Environmental Exposure & Risk, National Recommended Water Quality, Contaminated Sediments, Chemistry, Monitoring/Modeling, Environmental Monitoring, Engineering, Chemistry, & Physics, Environmental Engineering, monitoring, cyanide, contaminated sediment, chromatographic

Progress and Final Reports:

[Original Abstract](#)