Public Safety

Clear and Potential Danger

Water soluble cyanide salts can safely be placed on the list of chemicals that need to be handled with extraordinary care. Hydrocyanic acid, i.e. hydrogen cyanide in aqueous solution, has a pKA of approximately 9.2, which means that, even at neutral pH, cyanide in solution is mainly present as undissociated hydrogen cyanide (IUPAC: formonitrile). HCN is a highly toxic gas that is listed as a chemical warfare agent and was previously used as a rodenticide. On the more productive side, cyanides are widely used in industrial applications due to their capacity to form useful products when combined with either organic or inorganic compounds. For example, cyanide compounds are widely used in the production of polymers, and in the mining of silver and gold. This means that cyanides can potentially be emitted into the environment through process waste water. Once in the environment, cyanides can enter surface and ground water systems and ultimately become present in our drinking water. A further threat, which has more recently gained the attention of authorities, is the possibility of deliberate terrorist attacks on drinking water sources. All of the above warrant regular monitoring and uniform methods of analysis to ensure public safety. A method based on Headspace GC/MS (HS-GC/MS) was recently promulgated by the US EPA. The method ensures that cyanide concentrations well below legal limits can be determined quickly and accurately using instrumentation that includes automated sample preparation.

KCN (potassium cyanide) and NaCN (sodium cyanide) are salts of hydrocyanic acid better known as hydrogen cyanide (HCN). HCN is among the strongest and fastest working poisons. The lethal dose is around one to two milligram per kilogram body weight and can be incurred by either oral ingestion or inhalation.

Seconds after ingesting just 120 to 250 mg of KCN or NaCN, the victim goes into shock. Breathing is initially difficult, then impossible and after approximately one minute the victim will lose consciousness. Even immediate medical assistance will typically not help. The patient will die of acute respiratory paralysis within minutes.

Complexing agent of the first order

Pure hydrogen cyanide (HCN) is a colorless, highly volatile liquid with a boiling point of 26 °C and a characteristic bitter almond odor. Not all humans are genetically predisposed to being able to smell HCN, though. Even if a person is able to detect the smell, their olfactory sensory system will quickly cease to function when exposed to high HCN concentrations. The toxic effect of cyanide is mainly based on its ability form stable complexes with metals such as iron (III), which is charged with the vital task of making oxygen available to cells inside the human body. As a consequence, cyanide blocks transport of oxygen into the cells and leads to what is sometimes referred to as inner asphyxiation.

To a certain degree, this process can be reversed through appropriate and prompt theraputic counter-measures. In addition, humans can metabolize small amounts of cyanide enzymatically in the liver and dispose of the metabolites through the urinary system, which is why we can eat apple pits without worrying even though they contain minute amounts of cyanide. Other products such as bitter almonds, peas and beans contain cyanogenic glycosides, from which HCN can be formed in the body through enzymatic or chemical hydrolysis.

As an aside: Not all cyanide compounds are toxic, potassium ferrocyanide, for example, is not. The chemical forms relatively stable complexes and is used as a stabilizer. In the European Union (EU), potassium ferrocyanide is known as food additive E536, but can only be used as an additive in table salt products and only at very low concentration.

The most dangerous cyanide salts are those formed with alkaline metals or alkaline earth metals. These salts are highly soluble and are often used to extract raw silver or gold from ground ore. This process is known as cyanide leaching. In the gold-extraction process, ore is ground, mixed with water. Cyanide is then added to "leach" the gold out, precious metals form complexes with cyanide and are extracted into solution. Even though the extraction is performed in a closed loop process, residues of the highly toxic cyanide leaching solution can occasionally spill into the environment where they contaminate soil, surface and ground water. An example of worst case damage by a cyanide spill was seen in January 2000, when heavy rainfall combined with melting water run-off damaged a retaining wall at a gold extraction processing plant in Baia Mare, Roumania. According to estimates, more than 100 000 m^3 of poisonous waste water flooded into the Lupes, Somes and Tisza rivers, tributaries to the Danube, killing all life.

The need to monitor Cyanide in drinking water

Poisoned water bodies sooner or later regain their equilibrium thanks to the work of Mother Nature: Cyanide is oxidized to nitrogen and carbon dioxide. In chemical processes, the reaction is accelerated by adding sodium hypochlorite (NaOCl) or hydrogen peroxide (H_2O_2). Without help from human hands, the process takes longer and time is always of the essence.

Even limited amounts of cyanide ingested through our food or drinking water over years can accumulate in our bodies and can cause significant damage to our health. The United States Environmental Protection Agency (U.S. EPA) has therefore established a Maximum Contaminant Level, (MCL) which must not be exceeded. The MCL for cyanide is 0.2 milligram per liter or 200 parts per billion (ppb). The German drinking water regulation (TrinkW2001) specifies a maximum concentration of 0.5 mg/L. If this concentration level is exceeded, the water supplier must take measures to ensure adequate consumer protection.

HS-GC/MS as the method of choice

To determine the concentration of dissolved cyanide in drinking water, the most suitable technique is headspace gas chromatography using mass selective detection (HS-GC/MS). The technique captures all cyanide compounds that form HCN under acidic conditions. Jim Eaton, Ph.D., from the H&E Testing Laboratory in Augusta, Maine has recently established an official test method for the State of Maine. Method ME355.01 is entitled *Determination of cyanide in drinking water by gc/ms headspace analysis*. The method was originally made available by the Centers of Disease Control (CDC) for the analysis of cyanide in whole blood, a method that is part of the technology transfer group at CDC involved with chemical terrorism. Method ME 355.01 has now been promulgated by the US EPA. The method involves the following steps:

Samples are taken in 40 mL brown glass vials. 1 mL of a 1 M NaOH solution is added to preserve the sample, which is then stored at 4 °C in darkness until it is analyzed. The sample must be analyzed within seven days. Prior to the analysis, a 2-methyl aniline solution is added to the preserved sample. If the sample turns yellow it is discarded. To ensure efficient and accurate analysis, a suitable autosampler capable of automated sample preparation should used; the Dual Rail PrepStation version of the GERSTEL MultiPurpose Sampler (MPS) is listed in the official method. The MPS PrepStation is a two-in-one autosampler, capable of performing both headspace sampling and liquid handling. The liquid handling steps can include, for example, the addition of an internal standard, a reagent, or a diluent. A standard GC/MS system was used for separation and determination of the analytes.

Sample preparation: From each sample collection vial, a 1 mL aliquot is taken and transferred to a 10 mL standard headspace vial, which is capped. The prepared headspace vials are then transferred to the MPS PrepStation for analysis. All further steps are performed automatically, set up by mouse-click through the GERSTEL MAESTRO software, fully integrated with the GC/MS software. Just one method and one sequence table conveniently control the entire process, from liquid handling sample preparation to the HS-GC/MS analysis. In the MAESTRO PrepBuilder, the user can easily set up all necessary steps by selecting them from a drop down menu and adding them to the method. To ensure maximum efficiency and sample throughput, the PrepAhead feature enables overlapping sample preparation of up to 6 samples while the current analysis is in progress. All samples are introduced to the GC/MS system just as it becomes ready after analyzing the preceding sample, which means that the GC/MS system is never idly waiting for the next sample to be prepared.

Back to the method: The MPS automatically adds 50 µL internal standard, an aqueous solution of $K^{13}C^{15}N$, to the sample, followed by 200 µL ascorbic acid and 200 µL phosphoric acid, which are added to release HCN. After thermostating the headspace vial for four minutes at 60 °C, the MPS draws an aliquot of the headspace in the vial. The aliquot is introduced to the GERSTEL Cooled Injection System (CIS) inlet, focusing the analytes at -10 °C. After approximately 1.5 minutes, the CIS is quickly heated to 220 °C and the analytes are transferred to the GC/MS system for determination.

Following conditions were selected:

GC column:	PLOT Q Column from Agilent, part number: #19091P-Q04 or equivalent
Carrier gas:	Helium (1.1 mL/min), constant flow
Oven:	110 °C (0 min) – 4 °C/min –130 °C (0 min) – 99 °C/min – 250 °C (1.79 min)
MS Mode:	Selected Ion Monitring mode: (SIM)
Mass traces:	0, 29 (internal stadard), m/z: 27, and 26

Round robin

The method was tested by three independent laboratories. The following sample types were analyzed by each laboratory, each type was laced with 50 and 200 ppb cyanide respectively:

- Reagent grade water
- High salt concentration water
- Drinking water with high Total Organic Carbon (TOC) level.

All three laboratories reported results that were well within the requirements, confirming the usefulness of the method.

Method ME355.01 was specifically developed to require only small amounts of reagents and standards thus minimizing the potential hazard to both the environment and the analyst.

For more information

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