Title: Development and application of a new GC-MS method for the determination of cyanide using the highly selective derivatisation reagent 1,2,3,3-tetramethyl-3*H*-indolium iodide (TMI).

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Abstract:

Cyanide is known for its extremely high toxicity; however, many industrial chemical processes, such as the plating industry and manufacture of synthetic resins, require cyanide. Because cyanide is relatively easily obtainable, it has often been used in homicides and suicides, where in several cases it has been mixed into beverages. Measuring the cyanide concentration in blood is extremely important for estimating cyanide poisoning. Pentafluorobenzyl (PFB) derivatization tandem gas chromatography-mass spectrometry (GC-MS) is frequently used to derivatize cyanide compounds specifically. However, this method can be contaminated by equipment and is not sufficiently sensitive for identification by electron ionization. Thus, we aimed to develop a new GC-MS method to solve this problem. We develop a specific derivatization gas chromatography–mass spectrometry (GC-MS) method for cyanide using 1,2,3,3-tetramethyl-3H-indium iodide (TMI) as the derivatization reagent. Compared with the PFB derivatization, this method exhibited higher sensitivity and less column contamination and degradation, indicating its usefulness as an alternative. The derivative compounds were synthesized and characterized using 1H nuclear magnetic resonance (NMR), 13C NMR, and Fourier transform infrared (FT-IR) spectroscopy. The high selectivity of this derivatization for cyanide is supported by calculations and activation energy comparisons. In addition we applied this method to pure water, green tea, orange juice, coffee cafe au lait, and milk. The derivatization was completed in 5 min at room temperature for each beverage, showing that the selective

ion monitoring analysis is linear over the range 0.15–15 μM ($R^2 > 0.998$), with a detection limit of 4–11 μM. The intraday precision and accuracy ranged from 1.1% to 8.8% and from −10.3% to 12.1%, respectively. The interday precision and accuracy ranged from 3.5% to 12.8% and from −12.7% to 7.0%, respectively. We anticipate that this method can become widely used in forensic toxicology analysis. The TMI derivatization method developed herein has excellent potential for simple and high-sensitivity detection of cyanide. Moreover, the demonstration of TMI derivatization for cyanide in beverages shows effective detection of cyanide in leftover beverage samples. Analytical techniques capable of derivatizing high-matrix samples, such as beverages, can help to determine the cause of poisoning in cyanide-induced incidents. This method was included in the Japanese quasi-official Standard methods of analysis in poisoning with commentary.

Biography:

Dr. Keiji Nishiwaki joined Kinki University as a research associate in 1997 and became an associate professor in 2024. His research has ranged from computational chemistry, synthetic chemistry, medicinal chemistry and the development of detection reagents.