Avoiding Cyanide Compliance Problems

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Abstract

A recent survey of the metal finishing industry revealed that over 75% of the shops are still using cyanide.[1] Interestingly enough, cyanide compounds are also widely used in nonplating applications. For instance, road salt and Prussian Blue Dye contain cyanide. This paper reviews the alkaline chlorination process used to destroy cyanide and the procedures used to analyze for cyanide. Of special interest is a new, high speed analyzer[1] which simplifies testing for total cyanide. This analyzer can be used to screen samples and quickly spot problems with wastewater treatment before permit violations occur.

Why Use Cyanide?

For all the bad publicity it gets, cyanide might as well be "public enemy #1." After all, cyanide is used in the gas chamber and a few years ago some crazy person put it in Tylenol. Recently the newspapers told about a plater who was fined and put in jail for dumping cyanide plating solution into the Chicago River. Why, then, would anyone in his or her right mind want to use products that contain cyanide? Simply because in many cases we don't have a choice. For instance, most gold and silver electrical contacts used in telephones and computers are still plated in cyanide baths. We've grown accustomed to these conveniences and most people aren't ready to give up these "creature comforts." Although excellent progress has been made in developing "cyanide free" products, cyanide chemistries still must be used in many processes. Many times the "cyanide free" replacement products don't work as well. Some processes such as bright brass electroplating are not even available in "cyanide free" formulations. Also, deposits from cyanide formulations have good ductility and can be formed after plating.

In addition, some cyanide compounds such as ferrocyanides are quite stable and have very low toxicity. The uses of ferrocyanide are wide spread and include road salt and Prussian Blue Dye.

Protecting Our Environment

We have made great strides in making our environment a better place for our children and grandchildren to live. However, regulated materials such as cyanide are going to be around for a long time. Therefore, unless an important environmental benefit can be demonstrated, these necessary chemicals should not be regulated out of existence. After all, gasoline, electricity, and natural gas pose just as great a health hazard as cyanide.

What we need are better methods to determine the toxicity and analyze the concentration of cyanide. For instance, ferrocyanide (complexed cyanide) is much less toxic than sodium cyanide (free cyanide) which is amenable to chlorination. However, the laboratory test for ferrocyanide (commonly called total cyanide) is very long and complex. A typical total cyanide analysis takes about two hours and costs between $50 and $75. We need a faster method of analysis that is accurate, low cost, and not prone to common interferences.

Also, many substances are known to cause a false positive test for cyanide. In one case, a large Midwestern plumbing goods manufacturer had to work day and night to isolate such an interference. The problem turned out to be a defoamer that was being used in one of the processes. However, troubleshooting this problem would have been much faster and easier if a rapid test for total cyanide was available.

The key point that the authors want to make is you can avoid cyanide compliance problems without eliminating cyanide from your processes. This is possible because existing treatment technology is reliable and has been proven to consistently destroy cyanide. Also, an improved analytical technique, which makes frequent monitoring possible and simplifies troubleshooting has recently been developed. These technologies are discussed in the following paragraphs.

Destroying Cyanide

Treating cyanide wastes has come a long way since the alkaline chlorination process was developed by the American Electroplaters and Surface Finishers Society (AESF) in the 1950's. Most chemists will agree that "free" cyanide is easily destroyed by oxidation with chlorine. The "free" cyanide is reacted with chlorine at pH 11.0 to form cyanate. Cyanate is a non toxic material which is not regulated. In fact, allyl isothiocyanate naturally occurs in horseradish and helps give this condiment its distinctive flavor.[2] However, if desired, cyanate can be oxidized to carbon dioxide and nitrogen by lowering the pH to 8.5 and reacting with additional chlorine.

Usually the alkaline chlorination process is automated with pH and ORP controllers to monitor the reaction and make additions of the reagents. However, there are some limitations to this process. For example, the maximum concentration of "free" cyanide that can be treated is 1,000 mg/L. Also, cyanide that is complexed with gold, iron, mercury or cobalt is not destroyed by alkaline chlorination. Although most of these complexes are formulated for plating applications, iron or ferrocyanide is not. Ferrocyanide is formed when steel parts dissolve in the plating bath and iron combines with free cyanide. This complex is very stable and normally is the primary constituent of "total" cyanide.

Fortunately, the ferrocyanide complex can usually be removed by hydroxide precipitation. First, the "free" cyanide is completely destroyed by alkaline chlorination. Then, the pH is lowered to about 8.5 and the complexed cyanide precipitated out as a hydroxide. In addition, it may be necessary to add zinc sulfate if zinc is not present in the wastestream.

How Cyanide is Analyzed

Most total cyanide is analyzed using the "Standard Methods" distillation process (U.S. EPA Method 335.2).[2] The cyanide in the sample is released from its complexes by reflux distillation with a strong acid in the presence of the magnesium ion. Cyanide is released as hydrogen cyanide gas and is trapped in a scrubber solution of sodium hydroxide. This solution is then colorimetrically analyzed for cyanide using chloramine -T and pyridine - barbituric acid.

Cyanide amenable to chlorination, or "free" cyanide, is analyzed in much the same manner (U.S. EPA Method 335.1).[2] The sample is split into two portions and a total cyanide analysis is performed on one of the portions. The second portion is treated with calcium hypochlorite which destroys the available cyanide. Next, ascorbic acid is added to destroy the excess hypochlorite. Then the treated sample is analyzed for total cyanide. The difference between the two results is defined as "cyanide present in the sample which will be decomposed by chlorination."

Another test for "free" cyanide is called Weak Acid Dissociable cyanide (WAD). This method is similar to the total cyanide method described but is modified by using weaker acid and lower temperature in the distillation step. A standard colorimetric test is used to determine the cyanide concentration.

Unfortunately, there are several limitations to these cyanide testing procedures. The analysis is complicated and time consuming. For example, the time required is about two (2) hours for a single test. Moreover, the test is costly (usually $50 to $75) and must be done by a highly skilled technician. One of the greatest limitations is interferences. There are known substances, such as strong oxidizers and reducing agents which cause interferences and can result in false readings.

New Technology for Cyanide Analysis

A new "flow through" cyanide analyzer had been developed. This method is based on flow injection with gas diffusion and uses amperometric detection. The sample is injected into a carrier stream much like gas or liquid chromatography. Next, the sample is acidified and hydrogen cyanide gas is released. The stream passes into a gas diffusion cell where the hydrogen cyanide diffuses through a hydrophobic membrane into a flowing alkaline receiving stream. The "free" or WAD cyanide is measured amperometrically and the results plotted on a computer. Also, since the data is retained in the processor's memory, reports are easily generated.

Total cyanide is measured in much the same manner. However, in addition to this process, the acidified sample passes through a ultraviolet (UV) digester. The UV irradiation breaks down the metal-cyano-complex bonds and liberates hydrogen cyanide.

The primary advantage of a "flow through" analyzer is speed. The time required to analyze for "free" and total cyanide is three and six minutes, respectively. Also, the cost per test is low and the precision and accuracy is comparable to standard methods. Table I shows the results of some tests run on laboratory standards. Also, the cyanide tests run on the wastewater matrix have good spike recoveries as illustrated by the effluent study shown in Table II. However, there are some limitations to this new technology. The analyzer is more expensive than conventional equipment such as distillation and colorimetric analysis, but, when one considers the cost savings of labor, production downtime and possible fines, the cost for "leading edge" technology is easily justified. Unfortunately, the unit has not yet been approved by the U.S. EPA for reporting purposes, but can be used for process control.

Cyanide Standard Study

Standard Concentration (mg/L)	Total Cyanide (mg/L)
Blank (deioninzed water)	0.0005
0.004 Laboratory Standard	0.005
0.040 Laboratory Standard	0.042
0.120 Laboratory Standard	0.122
0.345 Commercial Standard	0.326

Table 1

Wastewater Effluent Study

Spike Concentration (mg/L)	Total Cyanide (mg/L)	% Recovery
0.040 Spike on Composite	0.041	102
0.040 Spike on Composite	0.036	90
0.040 Spike on Composite	0.035	88

Table II

Improved Quality Control and Troubleshooting

Most wastewater treatment systems do not run "trouble free" 100% of the time and the alkaline chlorination process is no exception. Usually, the most frequently run "QC" check on this process is for "free" (residual) chlorine. In theory, if we have free chlorine (blue color on a starch iodide test paper) then all the cyanide has been destroyed. Unfortunately, this test does not tell us anything about the concentration of complexed cyanide which is not amenable to chlorination.

For instance, let us consider the case of a large West coast job shop using several cyanide plating processes. The new analyzer was used to routinely test the effluent every two hours. When an unexpected high free cyanide concentration was measured, the technician checked the alkaline chlorination process. And, a problem was discovered with the chlorine supply system. The cyanide analyzer was also put to the test at a large Midwestern plumbing goods manufacturer. There is a good demand for brass plated hardware; and consequently, the plating process runs between 100 and 120 hours per week. Total cyanide was routinely analyzed three times each week using Standard Methods. Whenever a cyanide sample was run for "reporting purposes", five tests were performed which included the blank, standard, sample, duplicate and spike recovery test. In fact, a whole day was devoted to running nothing but cyanide analyses.

Also, occasional problems would arise with the cyanide treatment process. These problems were difficult to isolate because the time delays that were required for analysis. Only three distillation units and one chemist were available for running the cyanide tests. Consequently, when the company learned about a portable "flow through" analyzer for cyanide, they were eager to test this equipment "on site."

The performance of the analyzer was exciting. Tests which previously had taken all day (9) were performed in one hour. The test results correlate well with standard methods performed on the same samples. Now the cyanide destruct process may be monitored several times per shift and as easily as checking pH. This allows management to take corrective action before problems reach the crisis stage. Noncompliance situations are avoided, as well as, costly production downtime.

Conclusion

In summary, you can avoid cyanide compliance problems without eliminating cyanide from your processes. Wastewater treatment technology for destroying and removing cyanide is practical and well proven. However, these processes must be checked frequently to make certain they are performing properly and a new, portable analyzer may be of help. The ability to analyze cyanide from various waste streams results in better control of one of the most environmentally sensitive and highly regulated compounds in our industry.

Pollution control laws are being aggressively enforced with large fines and even jail terms. Routine testing will allow for better control of the cyanide destruction process and help prevent noncompliance situations. Not only will management have increased confidence that the wastewater treatment process is working properly, but they will also gain peace of mind.

References

[1]

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[2] Code of Federal Regulations, 40 CFR 413.14

[3] Standard Methods for the Examination of Water and Wastewater. American Public Health Asosciation, Washington D.C., 1992, p. 4-27 to 4-31.

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