

Advice & Counsel

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Cyanide-ATC Headaches

Over the last six months, there seems to have been a rash of cyanide-amenable to chlorination (CN-ATC) problems, because several phone calls and personal conversations have gone along these lines:

Dear Advice & Counsel,

I have worked extremely hard over the last year to resolve violations on cvanide amenable to chlorination that our POTW has issued to us. The fines are starting to get really serious, and my boss is all over me to improve the wastewater treatment system. The trouble is, I can't get consistent analytical results, even on the same sample. I recently sent split samples to two other laboratories and so did our **POTW. Guess what? All four** laboratories could not agree on the analytical results. Two labs found us in compliance (one found no CN-ATC at all), while two labs said we were in violation. One of the labs that found us in violation obtained a reading as high as 23 ppm!

What the)(&@!\$)(&@\$% is going on here?

Signed, CN-ATC Headache #345

Dear Headache,

First, you should realize that you are not alone with this problem. Numerous companies and POTWs are wrestling with this issue at this time. The answer is that you probably have no violation, because the laboratories performing the analysis have no viable method of measuring cyanide amenable to chlorination. The prescribed methodology is seriously flawed.

Let's start at the beginning. The U.S. Environmental Protection Agency (EPA) promulgated CN-ATC as one of two alternate parameters on cyanide for compliance by metal finishers, the second being CN-T (total cyanide). Because cyanide compliance is required "at the point of treatment," however, many metal finishers who treat cyanide wastewater containing complexed cyanides (especially iron cyanide) have a very difficult time complying with the total cyanide limit of 1.2 ppm (daily max.) and 0.65 ppm (30 day avg.). After chlorination, wastewater containing iron cyanides (K_3 (Fe(CN₆) and $K_4(Fe(CN_6))$ typically can run from 8–30 mg/L of total cyanide, even if a large excess of chlorine is employed, as iron cyanide complexes are essentially indestructible with chlorine.

The discharger, therefore, petitions the POTW to allow for the alternate regulated parameter of cyanide amenable to chlorination (0.86 mg/L daily max. and 0.32 mg/L 30 day avg.), and here is where the "fun" begins.

All analytical procedures are subject to "imprecision." In other words, a perfectly precise analytical procedure will not yield the same result each time it is used on the same sample. The cyanide amenable to chlorination procedure has numerous factors that yield imprecision within the same laboratory, and also from one laboratory to the next. *This imprecision can easily lead to violations for discharges that are actually in compliance.*

First, cyanide amenable to chlorination is a mathematical result of subtracting two total cyanide analyses, one performed on the sample in the "as received" condition, and one performed on the sample after the sample is chlorinated by the laboratory analyst. Theoretically, both analyses should yield the same answer on a sample that contains no amenable cyanide, but the imprecision can yield some "interesting" results, including negative numbers.

For example, a sample that contains no cyanide amenable to chlorination, but contains 20 mg/L of total cyanide (iron complex). A standard deviation of five percent on 20 mg/L yields a second analysis that can be 19 mg/L, yielding a CN-ATC result of 1 mg/L (violation).

Independent Evaluation EPA hired a contractor to evaluate seven analytical procedures for cyanides (EPA-600/4-83-054 dated October, 1983). The following is the contractor's comment on the CN-ATC analytical procedure currently used to determine compliance:

"5.7.3 Conclusions—The method of analysis 'Cyanides Amenable to Chlorination,' was originally designed to indicate the treatability of cyanides by the alkaline chlorination process. It has become apparent during this study that this method exhibits a number of deficiencies. There are primarily two major areas of concern; these are (a) the method is subject to a number of interferences, and (b) the method is unable to definitely classify some of the cyanide compounds studied as either treatable or not treatable by the alkaline chlorination process. This latter problem is most apparent when one attempts to classify the compounds Hg(CN)₂, Ni(CN)₂, $K_{2}[Hg(CN)_{4}]$, and $K_{2}[Ni(CN)_{4}]$; in these cases, the percentage of the compound chlorinated varies over a wide range and is directly dependent on the initial concentration of the compound in the sample. It should be possible to alleviate some of these problems through a more judicious choice of chlorination conditions and/ or digestion-distillation procedures.

"5.7.4 Recommendations—Because of the widespread use of the EPA-ATC method, its deficiencies should be corrected. A different total cyanide method should be used to overcome the interference problems (see Section 4.3). An evaluation to determine the most efficient chlorination conditions is also recommended."

It is unfortunate that as of this date, the advice of this contractor has not been followed. The result is that some companies may be paying rather heavy fines, possibly for no real reason.

There is Another Test

There's more. There are actually three "official" methods for analyzing total and amenable to chlorination cyanide: ASTM D 2036 Method B, EPA Method 335, and "Standard Methods for the Examination of Water and Wastewater (19th edition) Method 4500-G" (shortened to Standard Methods in the rest of this article). Between these three procedures, there are variations in glassware, reagents, and methods of compensating for interferences. The chances of two laboratories obtaining the same results by using different methods on the same sample are remote.

Further, there is a lot of "slop" in each method. Let's examine the procedure for chlorinating the sample in the laboratory. Standard Methods offers the following instruction as part of the procedure:

"Divide sample into two equal portions of 500 mL (or equal portions diluted to 500 mL) and chlorinate one as in para b below." The other two methods contain similar language.

This means *the procedure allows dilution of the sample to be chlorinated*, something the metal finisher is not allowed to do by the regulations!

Dilution of the sample prior to chlorination in the laboratory can greatly affect test results. In fact, on a sample containing iron cyanide complexes, you get different levels of cyanide after chlorination if you dilute the sample than if you don't. Our laboratory investigated this by taking a sample of treated wastewater from a metal finishing company that plates brass on steel. Two portions were chlorinated in the laboratory, one at full strength, the second diluted 10 mL to 500 mL. The total cyanide results obtained on these laboratory chlorinated samples was:

• Full Strength: 62.5 mg/L

• Diluted 10/500: 45.0 mg/L

Obviously, a laboratory that chlorinates diluted wastewater will obtain high concentrations of cyanide amenable to chlorination and will be perfectly in compliance with the analytical procedure.

Each of the three procedures also offers the following instruction for

ensuring the elimination of excess chlorine after the chlorination of the sample is completed:

"Eliminate the residual chlorine by adding ascorbic acid (ASTM and EPA) or sodium arsenite solution (Standard Methods) or Sodium Thiosulfate (Standard Methods) until potassium iodide-starch test papers test negative for chlorine."

The EPA method indicates that an **excess** of 0.5 g ascorbic acid is to be added after the starch-iodide papers

test negative for chlorine. ASTM instructs the addition of 0.05 (50 mg) of excess ascorbic acid. Standard Methods provides no instruction for adding an excess of reagent for ensuring all the chlorine has been eliminated from the sample after the chlorination time is up.

Why is this important? During the cyanide analysis, excess chlorine remaining in the sample will leave the reflux flask and be discharged through the gas scrubber that contains the cyanide normally released by the sample. The gas scrubber utilizes a caustic soda solution. This results in perfect conditions for alkaline chlorination of the cyanide. The cyanide is destroyed in the gas scrubber, yielding low cyanide results on the chlorinated sample. This artificially low value is subtracted from the total cyanide to yield a high cyanide amenable to chlorination.

How can excess chlorine remain in the sample after chlorination, when the analyst removes it using one of the chemical reagents mentioned above? The answer is that an analyst following "Standard Methods" will add only enough reagent to neutralize the excess chlorine, based on potassium iodide-starch test papers. The problem is that these papers are inadequate for determining if all of the chlorine has successfully been eliminated. Our experiments have shown that the starch papers yield negative chlorine results, when as much as 2 ppm of chlorine is still present in the wastewater, and that 2 ppm of excess chlorine remaining in the sample can effectively eliminate a lot of cyanide:

When the above described wastewater, containing iron cyanide complexes, was analyzed with approximately 2–3 ppm of residual chlorine, the total cyanide after laboratory chlorination was less than 0.05 mg/L. The same sample yielded 62.5 mg/L when excess chlorine was totally eliminated.

With the above vagaries, is it any wonder that there is widespread disagreement as to what the real value of cyanide amenable to chlorination is on any given sample?

Research is Planned The good news is that EPA has included research into better analytical methods for cyanide and cyanide amenable to chlorination in its plans for the near future. Paul Shapiro of the Office of Research and Development has made this a high priority issue, based on responses to a recent survey of what issues the industry would like to have EPA research.

In the meantime, dischargers have the following options:

- 1. Install precipitation and clarification equipment for chlorinated cyanide wastewater, so that the monitoring point for compliance is after the iron cyanide has been precipitated.
- 2. All analytical parties involved with compliance sampling and analysis for cyanide amenable to chlorination must agree to chlorinate only full-strength wastewater in the laboratory and must ensure that all excess chlorine is eliminated by adding an excess of reducing agent, preferably the prescribed



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0.5 g of ascorbic acid recommended by EPA.

- 3. All analytical parties involved with compliance sampling and analysis should use the shortcut method (Standard Methods 3500-H) to cross-check all analyses for cyanide amenable to chlorination.
- 4. Dischargers may petition their control authority to substitute the Weak Acid Dissociable (Standard Methods 4500-I) or a similar procedure, termed the "Modified Roberts-Jackson Method for Analysis of Simple Cyanides," proposed by the EPA contractor referenced above. Each of these procedures eliminates the subtraction of two total cyanides, eliminates in-laboratory chlorination, and yields analytical results similar to cyanide amenable to chlorination.

The EPA contractor had this to say about the Modified Roberts-Jackson method:

"The modified Roberts-Jackson procedure for the analysis of simple cyanides is far superior to any other method investigated. The procedure provides a clear distinction between the different types of cyanides in solution and is relatively free of interferences. For those compounds that do interfere, other pretreatment methods have been described that will alleviate the problem. Most significantly, the interference from sulfide and thiocyanate have been completely eliminated. A deficiency of the procedure is the incomplete recovery of cyanide from mercury complexes."

There is precedence on your side, should you petition your control authority to allow the substitution of the Roberts-Jackson procedure for the CN-ATC method. It was a plater who provided me with a copy of the EPA report on cyanide methodology referenced above. He obtained it from his regional office of EPA, because he wrote a letter complaining that it was impossible for him to get any laboratories to even come close to agreeing on cyanide amenable to chlorination in his discharge.

Along with the report, the regional office of EPA recommended that this plater have his laboratory substitute the modified Roberts-Jackson method, and he hasn't had any compliance problems since. **PASF**