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# Method Comparison Study for Weak Acid Dissociation Cyanide Analysis

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Method comparison studies of two different methods for the analysis of weak acid dissociable (WAD) cyanide revealed analytical flaws and/or matrix interference problems with both procedures. EPA "draft" method 1677 using a Perstorp 3202 CN analyzer was compared to Standard Method 4500 CN I. It was discovered that the Perstorp analyzer produced more precise and more accurate results once appropriate and necessary procedural steps from the EPA draft method were modified. Comparison of these two methods, was based on "real world" samples collected from a mine-tailing solution. The mine-tailing solution contained high concentrations of cyanide and metals. Inconsistencies in method procedures were traced to sulfide interferences and high concentrations of WAD metals. Conclusions were based upon a large sample base collected from a mine site over a 90-day period.

## Introduction

The U.S. EPA/Pintail Systems Inc. Biocyanide Treatment Technology was demonstrated as part of the Superfund Innovative Technology Evaluation (SITE) Program at a mine site in Nevada. Science Applications International Corporation (SAIC), an EPA contractor for the SITE Program, performed an evaluation of this technology. The primary objective of the demonstration was to determine the effectiveness of this treatment technology at reducing weak acid dissociable (WAD) cyanide concentrations from a mine-tailing solution containing high concentrations of cyanide (250−350 mg/L) and various metals including As, Cd, Co, Cu, Fe, Mn, Hg, Ni, Se, Ag, and Zn ranging from 0.02 to 150 mg/L. Analysis of WAD cyanide performed by two separate methods, however, produced some important new information.

Requirements for this project mandated that cyanide concentrations be measured at an independent laboratory per common distillation techniques using an approved method, as recognized by the U.S. EPA oversight laboratory for the SITE Program, the National Risk Management Research Laboratory (NRMRL) in Cincinnati (e.g. SW-846 Method 9010 (*1*)). Because of the need to measure WAD cyanide, Standard Method 4500 CN I (*2*) for WAD cyanide was used as the definitive method for analysis. Developer requirements mandated that cyanide concentrations also be measured on a real time basis in order to ensure process optimization. For this purpose, a Perstorp 3202 CN analyzer was obtained for field determination of WAD cyanide (*3*). Using this analyzer (a ligand exchange/flow injection amperometric method of analysis), cyanide results could easily be determined within 1−2 h after sampling. The analyzer was simple enough to operate such that nonlaboratory professionals could learn to perform the analysis with minimal training. Because field Perstorp analyses and laboratory distillation analyses were both being performed, comparison of these two separate analytical procedures was possible. The traditional WAD cyanide procedure uses a weak acid distillation step that releases cyanide from defined metal complexes, which is subsequently distilled for analysis. The Perstorp procedure uses a ligand exchange reagent to chemically bind WAD metals, thereby freeing cyanide for analysis. This exchange reagent is provided by the instrument manufacturer for purchase and contains a proprietary composition of different compounds.

Samples were collected and analyzed for 90 days. Both methods of analyses were used on approximately one-half (45) of the samples. Differences noted between these two procedural data sets are the subject of this paper. It was expected that results from these two methods would be similar. The Perstorp analyses, however, after some modification appeared to be a more accurate representation of cyanide concentrations. The Perstorp analyzer and procedure, as presented in this paper, not only provides real time data but also provides more representative WAD cyanide results with less variability from matrix interferences, specifically high concentrations of metals in the sample stream.

**TABLE 1. Cyanide Summary Data (mg/L)[a]**

| | average | SD | low value | high value |
|---|---|---|---|---|
| **Process Feed** | | | | |
| laboratory | 240 | 61.1 | 115 | 378 |
| Perstorp | 263 | 48.1 | 210 | 388 |
| **Treated Effluent** | | | | |
| laboratory | 46.3 | 34.1 | 0.16 | 82.3 |
| Perstorp | 56.5 | 47 | 0.016 | 176 |
| **Laboratory Data** | | | | |
| process feed | 240 | 61.1 | 115 | 378 |
| control effluent | 256 | 44.8 | 191 | 390 |
| **Perstorp Data** | | | | |
| process feed | 263 | 48.1 | 209 | 388 |
| control effluent | 268 | 43.6 | 201 | 396 |

[a] See Figure 1.

## Experimental Section

Three sample streams were evaluated as part of this demonstration. Streams that were sampled included an influent stream designated as the process feed sample stream and two separate effluent streams, the treated effluent and the control effluent. (i) The process feed sample stream (mine-tailing solution) contained high concentrations of metals and cyanide (see Tables 1 and 2). (ii) The treated effluent sample stream was located at the exit of the biotreatment process. This sample stream was the primary sample used for evaluation of the system being tested and WAD cyanide concentrations ranged from less than 1 mg/L to ap-

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**TABLE 2. Metals Summary Data for the Process Feed and Treated Effluent Streams[a]**

| metal | process stream | average (μg/L) | SD | low value (μg/L) | high value (μg/L) | process stream | average (μg/L) | SD | low value (μg/L) | high value (μg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| **As** | **feed** | **342** | **35.5** | **291** | **409** | **effluent** | **45.7** | **21** | **20.7** | **89.5** |
| **Cd** | **feed** | **42** | **33.4** | **17.3** | **118** | **effluent** | **3.31** | **0.999** | **1.95** | **4.4** |
| **Co** | **feed** | **146** | **131** | **38.4** | **482** | **effluent** | **57.4** | **18.2** | **21.6** | **107** |
| **Cu** | **feed** | **149 000** | **29 900** | **75 100** | **184 000** | **effluent** | **43 300** | **40 300** | **13 000** | **162 000** |
| Fe | feed | 1 480 | 860 | 630 | 3 320 | effluent | 1 970 | 1 760 | 881 | 8 340 |
| Mn | feed | 20 | 17.9 | 1.75 | 56.9 | effluent | 70.3 | 32.7 | 36.4 | 156 |
| **Hg** | **feed** | **173** | **21.2** | **142** | **223** | **effluent** | **5.76** | **3.81** | **1.2** | **14.3** |
| **Ni** | **feed** | **1 640** | **110** | **1 470** | **1 800** | **effluent** | **687** | **293** | **276** | **1 270** |
| **Se** | **feed** | **246** | **61.4** | **163** | **391** | **effluent** | **75.2** | **48.6** | **11.6** | **151** |
| **Ag** | **feed** | **902** | **700** | **267** | **1 980** | **effluent** | **38.9** | **69.8** | **4.9** | **230** |
| **Zn** | **feed** | **22 000** | **22 800** | **6 340** | **70 700** | **effluent** | **538** | **217** | **250** | **998** |

[a] Bolded values are metals that appeared to have reductions in concentrations between the process feed and treated effluent streams based upon the summary statistics presented in the table.

proximately 100 mg/L with lower concentrations of metals. (Tables 1 and 2 summarize cyanide and metals concentrations, respectively, in both these sample streams.) (iii) The control effluent sample stream was located at the exit of the control treatment process and was used to monitor nonbiological reduction of cyanide and contained high concentrations of metals and cyanide. Because this sample stream remained untreated, concentrations of both cyanide and metals in this sample stream were similar to concentrations in the process feed sample stream and should be considered similar in composition to the process feed.

A preliminary data validation procedure for the Perstorp analyzer was performed prior to the demonstration using samples from the mine site. This report was prepared for the U.S. EPA and evaluates the readiness of U.S. EPA draft method 1677 (*4*) for analysis of the previously described samples. Draft method 1677 provided the framework for the analytical procedure for the real time cyanide analyses using the Perstorp analyzer. Some critical changes were made to this method, as explained in more detail in the Results and Discussion section of this paper. The complete SOP used during this demonstration is available upon request.

Instrument calibration ranges for the Perstorp analyzer covered 0.5−5.0 mg/L, and a second calibration range of 0.05−0.5 mg/L was used when concentrations of cyanide were lower than 0.5 mg/L. The lower limit of quantitation was considered as the lowest acceptable quantifiable standard for this method. Estimated results below 0.05 mg/L were reported down to a detection limit of 0.01 mg/L. Sodium cyanide standards prepared with 0.01 M NaOH were used for calibration of the Perstorp analyzer. Process feed samples and control effluent samples were diluted 1:100 with 0.01 M NaOH. Each sample was filtered using disposable 10-mL luer lock syringes with filters. After filtration, the ligand exchange reagents provided by Alchem (now the official distributor of the Perstorp analyzer) were added to each sample. Once these reagents are added, samples can be analyzed immediately. Analyses are completed in approximately 90 s as described in the Perstorp 3202 CN instrument manual.

QC samples included a method blank with every set of 10 analyses or less, a field/filter blank run on a daily basis, and a ligand exchange reagent performance (LERP) standard (essentially a spiked blank required for analysis with the Perstrop instrument) run with each sample batch of 10 or fewer samples. The spiked blank concentration was commensurate with a standard concentration in the middle of the upper calibration curve (2 mg/L) and 10 times less for the lower calibration curve. Matrix spikes/matrix spike duplicates (MS/MSDs) at 3−5 times the native CN concentration spiked with $HgCN_2$ solution were also run with each sample batch of 10 or fewer samples. Method blanks were required to be less than the lowest quantifiable standard. The LERP standard was required to be within 15% of the calculated value. MS/MSD results were within 25% of the calculated value with an RPD of 25%. Batch samples associated with results outside these parameters were reported and included in the method evaluation but, as noted later in this paper, are considered to be questionable. Only one sample batch produced QC results outside these required parameters. Analyses by the distillation procedure were performed using Standard Method 4500 CN I.

## Results and Discussion

**Sulfide Interferences.** *Sulfide Concentrations below 10 mg/L.* Some demonstration samples contained very low milligrams per liter concentrations of sulfide as discovered by observation of the precipitate formed in the treated samples using the procedure noted below. The traditional sulfide test (lead acetate paper as described by Standard Method 4500 CN I) did not detect concentrations of sulfide at these lower concentrations. Once Perstorp samples were diluted and aliquoted into 10-mL disposable glass test tubes, samples were treated for sulfides using a 1% lead acetate solution. (The previously noted SOP describes the sulfide test used during this demonstration in more detail.) It is the author's opinion that the reason this lead acetate paper test has been a part of standard cyanide analytical methodology is because of the test's ability to detect sulfides at higher concentrations (well above 10 mg/L as tested during this demonstration). This is likely because the laboratory distillation procedure does not have interference problems when lower sulfide concentrations are present. While routinely used, none of the samples during the entire study ever tested positive for sulfides using this test; therefore, sulfide interference for the distillation procedure was not considered significant.

Lower sulfide concentrations, which were present in the test samples however, were a significant problem for the Perstorp analysis. Through various experiments using a sulfide solution of known concentration, it was discovered that the presence of sulfide in a sample (even at low concentrations of less than 10 mg/L) caused reported WAD cyanide concentrations using the Perstorp procedure to be in error. The interference was so great that detected values of sulfide were picked up at twice the sensitivity of cyanide. [Trace sulfide determination by amperometric methods has been previously documented (*5*).] Because of this problem, even though samples may have tested negative for sulfide using the lead acetate paper (below 10 mg/L), all Perstorp analyses were routinely treated for sulfides.

*Procedures Used for Elimination of Sulfide Interferences.* Initially, solid lead carbonate was used to eliminate sulfide interference. Lead carbonate is routinely used in the distillation procedure and is recommended by draft method 1677. The use of lead carbonate, however, presented two problems.

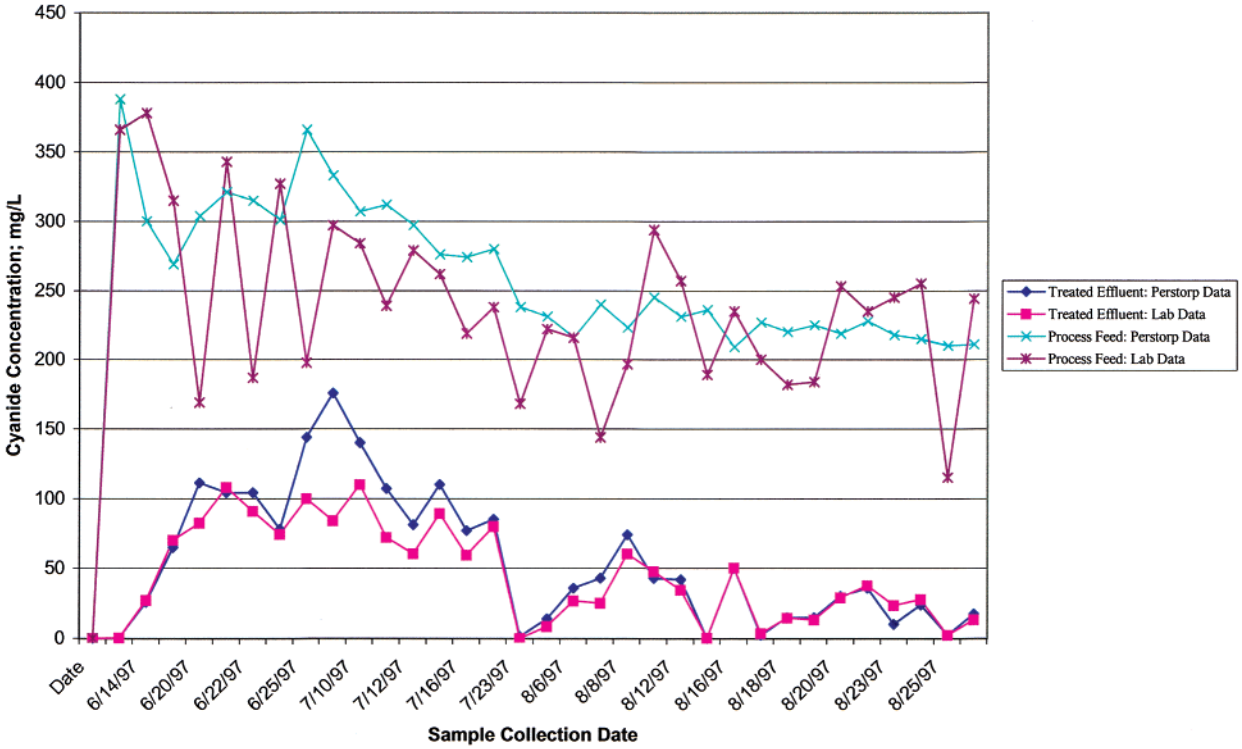


**FIGURE 1. Process feed and treated effluent data; laboratoy vs Perstorp.**

First, if too much lead carbonate is added, then it becomes an interference problem for the Perstorp procedure. Second and more important, lead carbonate does not easily dissolve in water. Because lead carbonate was not readily soluble, the lead carbonate/sulfide reaction required direct contact of the dissolved sulfide with the undissolved lead carbonate. Reaction kinetics for this type of reaction were slow and inefficient (even when left for several minutes it was evident that lead carbonate remained undissolved), thereby producing some lead sulfide precipitate but leaving a significant portion of unprecipitated sulfide to interfere with the cyanide analysis (as noted using sulfide solutions of known concentration). To solve this problem, a lead acetate solution was used to form the lead sulfide precipitate in a much more efficient reaction as was evidenced by almost immediate "dropping out" of lead sulfide. This presented a different problem.

The Perstorp analytical procedure uses a ligand exchange reagent to chemically bind WAD metals such as Hg, Mn, Ag, etc., thus releasing free cyanide for analysis. Metals that are considered to form "strong" cyanide complexes such as ferric cyanide are not chemically bound to the ligand exchange reagent. (See draft method 1677.) Hg and Ag are among the metals that appeared to be drastically reduced as result of treatment, refer to Table 2, and are therefore the subject of interest in regards to both method 1677 and the distillation procedure.

The process feed samples contained high concentrations of metals (Table 2). If there was too much lead acetate available in solution, the addition of the ligand exchange reagent for chemically binding the metals noted above and freeing cyanide for analysis proved futile. The ligand exchange reagent would be consumed by the excess lead acetate, and a yellow precipitate would form. This meant that cyanide bound by metals in the solution was not freed for analysis. Perstorp analytical results often showed significantly lower concentrations of WAD cyanide than laboratory results. This observation was noted early, and procedural corrections were instituted.

To eliminate this problem, the lead acetate solution was reduced to 1% lead acetate. This left a 10-fold excess of lead acetate available in solution for precipitation of sulfide if concentrations were as high as 10 mg/L. There was not enough excess lead acetate therefore to stoichiometrically bind all the ligand exchange reagent. This left excess reagent to capture metals from metal cyanide complexes defined as WAD complexes and free cyanide for subsequent detection. Using this procedure, sulfide interferences could be easily removed, and high concentrations of metals in the process feed were bound to the ligand exchange reagent, thereby ensuring that all WAD cyanide was freed for accurate analysis.

**WAD Cyanide Data Comparisons.** Two graphs, comparing laboratory and Perstorp data, are presented in Figure 1. These include a comparison of the treated effluent and process feed sample streams. Classical statistical analyses (e.g., paired *t*-test) were performed on these data to determine the significance of the results. As is sometimes the case, there was limited information that could be obtained using these analyses. The author therefore chose to present the data graphically (descriptive statistics) in order to more precisely represent the results of this study. It is the presumption of the author that these data comparisons show the Perstorp analytical procedure, modified to eliminate sulfide interferences, to be more accurate and more precise and subsequently a better method for determining WAD cyanide concentrations than the laboratory distillation procedure. The reasoning and analysis presented below along with the collected data provide the rational behind this conclusion.

*Treated Effluent Data Comparison between Laboratory and Perstorp Data Produced Similar Results (see Figure 1).* Because of the decision to present these data as a graphical comparison using descriptive statistics, a correlation coefficient was used to better quantify the results of this comparison. A correlation analysis was therefore used to determine how well one set of data would predict the result for the second set of data. This is a similar approach for determining analytical instrumentation response to a given standard. For purposes of comparison, the laboratory data was considered

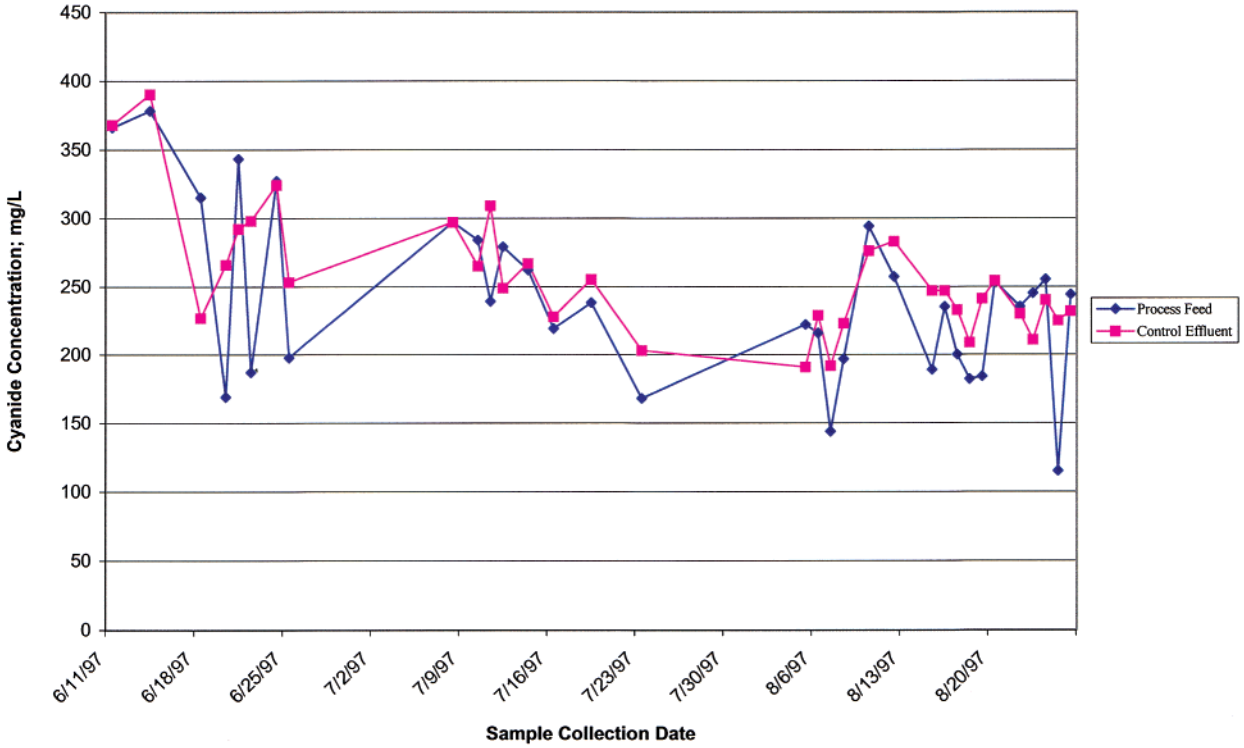


**FIGURE 2. Laboratory data; process feed vs control effluent.**

the standard or independent variable. The correlation coefficient for these two data sets was calculated as 0.9359. (The closer the correlation coefficient is to 1, the more significant the correlation.) Treated effluent results from the two different analyses therefore show that the Perstorp analytical procedure compares reasonably well to the standard laboratory analysis at least relative to the comparisons noted below. This is one of the primary discoveries made as a result of this study.

The low metals concentrations recorded in the treated effluent stream are important to consider when comparing these data (see Table 2). The few data points that appear different between these two data sets were collected when this sample stream had high concentrations of both metals and cyanide. [Note data collected between June 25 and July 16. When cyanide concentrations were high, metals concentrations were also high because of the inefficiency of the process being tested for reduction of cyanide. Process results showing high concentrations of metals corresponding to inefficient process operation can be found in the SITE Technology Capsule (*6*).] As discussed below, the high metals concentrations are the likely cause of the significant differences.

*Process Feed Comparisons between Laboratory and Perstorp Data Not as Consistent as Treated Effluent Data Comparison (see Figure 1).* The correlation coefficient between laboratory and Perstorp data for the process feed stream is 0.4837. This correlation coefficient is indicative of a much greater difference between these two sets of data than what is presented above for the treated effluent and therefore suggests that these two data sets were more dissimilar. Because all sample streams were treated in a similar fashion (collected, stored, and preserved under the same conditions) and because the same laboratory performed the distillation procedure, the observed difference is potentially because there is a difference in the sample stream being analyzed. Specifically, the treated effluent stream had lower concentrations of metals than the process feed stream because of the process's ability to significantly reduce metal concentrations in the effluent stream. It is believed that the metal–cyanide complexes are in fact the key to explaining why the Perstorp method out-performed the laboratory procedure.

Close examination of Figure 1 reveals that there are greater differences in the process feed data comparison than differences in the treated effluent data comparison. (There are a few striking differences in the treated effluent data comparison that are noted in the previous discussion and occur when the process was working less efficiently and both metals and WAD cyanide concentrations are high.) This difference is particularly evident when comparing the correlation coefficients noted above. This same scenario was noted when comparing the control effluent data stream, which was similar in composition to the process feed (Figures 2 and 3). Other than differences in cyanide concentration in the process feed and treated effluent streams, differences in metals concentrations are also significant. In fact, of the metals analyzed as part of this demonstration, all but two metals (Fe and Mn) showed 50–90% reductions between process feed data and treated effluent data.

*Comparison of Process Feed Data to Control Effluent Data.* Two separate comparisons are shown in Figures 2 and 3. The comparison of the laboratory analyzed process feed and control effluent data has a correlation coefficient of 0.7759. Comparison of the Perstorp analyzed process feed and control effluent data has a correlation coefficient of 0.9581. This comparison of correlation coefficients indicates that there is more variability between laboratory data than Perstorp data when comparing the process feed and control effluent sample streams. In addition, one can visually determine that the difference between the laboratory data comparison is greater than the difference between the Perstorp data comparison for these two sample streams (refer to Figures 2 and 3). Because variability is greater for the laboratory data comparison than for the Perstorp data comparison for two sample streams that are similar in nature and because the concentration of metals in these sample streams is also high, this is an additional confirmation that the Perstorp method is more consistent for measuring WAD cyanide when high concentrations of metals are present.

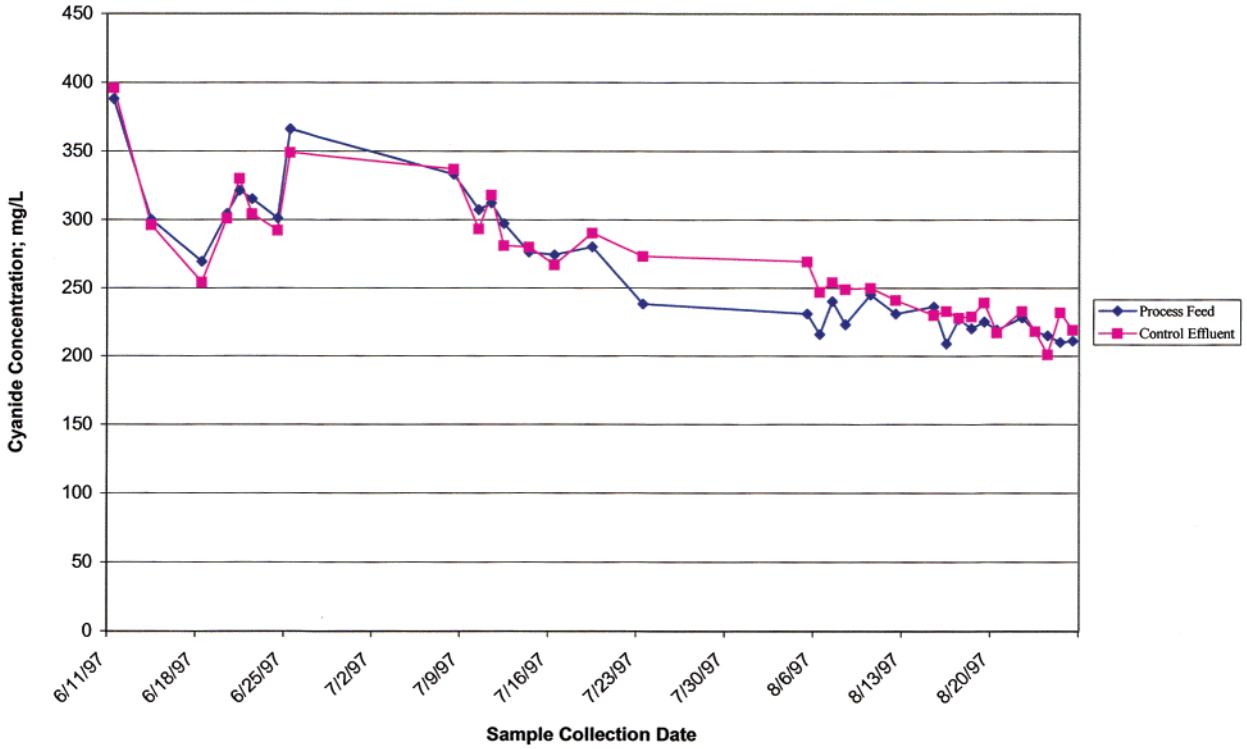


**FIGURE 3. Perstorp data; process feed vs control effluent.**

In summary, the above data comparisons suggest that the Perstorp analytical procedure modified to minimize sulfide interferences is potentially a more precise and accurate method for determining WAD cyanide concentrations as compared with the laboratory procedure, especially in the presence of high concentrations of metals. It is therefore the conclusion of this paper that high concentrations of metals in the sample being analyzed is the reason for the differences between cyanide concentrations noted above and that low concentrations of metals explain the similarities between treated effluent sample streams analyzed by the two different methods.

The traditional WAD cyanide procedure uses a weak acid distillation step that releases cyanide from defined metal complexes, which is subsequently distilled for analysis. The Perstorp procedure uses a ligand exchange reagent to chemically bind WAD metals, thereby freeing cyanide for analysis. The evidence above suggests that the ligand exchange reagent is more consistent (more precise and more accurate) in freeing cyanide from WAD metal complexes than the distillation procedure. This conclusion is not new or unique as this is similar to previous conclusions reached by Milosavljevic et al. (*7*). It is likely a result of the distillation procedure being affected by small undetected procedural changes from one run to the next affecting reaction kinetics.

There is an additional observation that also suggests that this theory is correct. Comparing all of the data points between Perstorp and laboratory data for the process feed and control effluent sample streams (both sample streams containing high concentrations of metals) and assuming 20% analytical variability as part of this method comparison, there are 17 data point comparisons that are greater than 20% different (relative percent difference). This would be a greater difference than expected based upon the QC data for both methods. Of these 17 data points, 15 show that the Perstorp analysis has a higher concentration of WAD cyanide. The two data points that are lower are on days when the Perstorp analysis had questionable QC results where LERP results did not meet specified requirements. Discounting these two points, 15 of 15 data points (100%) have higher WAD cyanide concentrations as determined by the Perstorp analytical method. (Limits for QC results are provided in previous paragraphs.) This evidence suggests that determination of WAD cyanide by the traditional laboratory data is suppressed in the presence of high concentrations of metals.

The reason the Perstorp analysis may have higher concentrations of WAD cyanide when concentration differences between these two methods are greater than 20% is likely the same reason noted above. The high concentrations of even weak and dissociable metals may be chemically binding cyanide, thereby preventing this same cyanide from being released by distillation and subsequently detected. Apparently, in some instances and also somewhat randomly, the laboratory procedure may not break some of the metal cyanide bonds within the WAD cyanide complex, which otherwise need to be broken in order to free the cyanide for analysis. These data therefore suggest that the ligand exchange/Perstorp procedure is more precise and accurate when samples containing high concentrations of metals are analyzed for WAD cyanide.

## Literature Cited


(1) U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Wastes*; SW-846, Method 9010; U.S. Government Printing Office: Washington, DC, 1986.

(2) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; Method 4500-CN; Lewis: Boca Raton, FL, 1989.

(3) *ALPKEM CN Solution Model 3202 Operator's Manual*. Part Number A001462; Available from ALPKEM, a division of OI Analytical, Box 648, Wilsonville, OR 97070.

(4) U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Wastes*; SW-846 Proposed, Method OIA-1677; 1998.

(5) Milosavljevic, E. B.; Solvjic, Lj., Hendrix, J. L.; Nelson, J. H. *Anal. Chem*. **1988**, *60*, 2791−2796.

(6) Pinatail Systems Inc. *Aqueous Biocyanide Process*, SITE Technology Capsule; EPA/540/R-00/501a; September 2000.

(7) Milosavljevic, E. B.; Solvjic, Lj.; Hendrix, J. L. *Environ. Sci. Technol.* **1995**, *29*, 426−430.



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