

THE EFFECT OF MULTIPLE INTERFERENCES ON THE DETERMINATION
OF TOTAL CYANIDE IN SIMULATED ELECTROPLATING WASTE
BY EPA METHOD 335.4

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INTRODUCTION

The U.S. Environmental Protection Agency approved test procedures for cyanide determination are listed in the Code of Federal Regulations 40, Ch.1, Pt.136, Appendix B, Table 1B. The test procedures are used for the reporting of results of analyses as required by the National Pollutant Discharge Elimination System (NPDES) permits. The methods listed for total cyanide in water all share similar chemistries and interferences. These interferences have resulted in many modifications of the procedures that are included in Standard Methods¹, ASTM², and the EPA methods.^{3,4} The application of these modifications requires prior knowledge of the interference. Procedures to remove the interferences generally work well when a single interference is present. However, when multiple interferences are present, the total cyanide methods produce questionable analytical results.

The objective of this study was to evaluate the performance of the method when applied to simulated waste effluent that contained known concentrations of cyanide and multiple interferences. Electroplating waste effluent was studied because there have been many problems reported by analysts for that waste, and because it was known to contain a large number of method interferences. In brief, the problems reported included low recovery of cyanide spikes, suspected false positive results, and poor precision for replicate analyses.

OVERVIEW OF THE CYANIDE METHOD

Method 335.4 consists of two discrete analytical steps: (1) MIDI distillation of an acidified solution into an alkaline collector, and (2) colorimetric analysis.⁴ In the first step, cyanide is converted to HCN at pH 1 by addition of sulfuric acid to the sample. The gas is purged from the sample solution into an alkaline absorber solution where it is stabilized as the cyanide anion. The purpose of this distillation step is to remove cyanide from method interferences that are present in the sample, and stabilize it in a clean matrix. The second step is a colorimetric analysis procedure using pyridine-barbituric acid reagent to form a colored adduct.

The MIDI distillation and analysis procedures were used to the extent possible. MIDI distillation was performed with an automated, 10 sample, temperature-controlled, heating block (Cyan-Ten, Andrews Glass Co.). Analysis was performed with an automated flow injection analysis colorimetric analyzer (QuikChem AE, Lachat Instrument, Inc.).

METHOD INTERFERENCES

Electroplating industry waste contains many interferences that affect the cyanide method. Table 1 contains a list of nine types of interferences that have been reported to be problematic in electroplating waste. Note that while some of the interferences listed are discrete chemicals (e.g. sulfide, thiocyanate, carbonate), others include entire categories of compounds (e.g. oxidizers, surfactants, metals). In the design phase of this study, we

performed preliminary experiments to identify five of the most significant interferences. We did not include metals in this testing because they were being studied separately. The five interferences selected were sulfide, hypochlorite, bisulfite, formaldehyde, and thiocyanate.

For some interferences, Method 335.4 recommends interference recognition tests ("spot tests") and/or interference removal methods. This information is summarized in Table 2, with "YES" listed if the method recommends a spot test for that interference, and "NO" if no test is recommended. The active reagent in the interference removal method is also listed if one is recommended by the method. Note that thiocyanate and bisulfite do not have spot tests. However, the Standard Methods 4500-CN procedure recommends addition of lead carbonate to the absorber tube of samples with sulfur-containing compounds, and thus lead carbonate is added to samples with thiocyanate and bisulfite.

RANGE FINDING STUDIES

In order to design the multiple interference study, it was first necessary to perform a series of range finding experiments to identify the most significant interferences and estimate the range of concentrations over which the interference had a measurable effect on cyanide recovery. The range finding studies were very limited tests of each interference individually. Typically, five solutions were prepared in duplicate with either 0 or 100 $\mu\text{g/L}$ CN and a series of concentrations of a single interference; in some cases, more than five solutions were prepared and tested. In order to determine if the recommended interference removal method improved the recovery of cyanide, we treated some samples with the interference removal reagent and did not treat others. Samples were then distilled and analyzed according to Method 335.4. Results are shown in Figures 1 to 5 for sulfide, hypochlorite, formaldehyde, bisulfite, and thiocyanate, respectively. Samples designated as "Treated" were treated with the interference removal method; those designated "Untreated" were not. Data presented in the figures represent measured cyanide based on instrument calibration with undistilled KCN standards, and have not been blank-subtracted or otherwise corrected.

In the case of sulfide (Figure 1), samples contained either 0 or 100 ppb ($\mu\text{g/mL}$) CN, and 0, 7.8×10^{-5} , 1.6×10^{-4} , 3.1×10^{-4} , or 6.3×10^{-4} M sulfide. Treated samples contained lead carbonate in the absorber tube; untreated samples did not. Results shown in Figure 1 illustrate that:

(1) reagent blanks (0 ppb CN, Untreated) contained very little cyanide (approximately 2 ppb CN); (2) "Treated" blanks (0 ppb CN, Treated) had high measured cyanide (approximately 15 ppb CN); (3) In the absence of interference or treatment (100 ppb CN, Untreated, 0 Sulfide), cyanide was recovered at approximately 80% of nominal, but when sulfide was present (100 ppb CN, Untreated, $1.6\text{E-}04$ Sulfide) the recovery decreased to approximately 50% of nominal; (4) Treated samples generally had higher recovery of cyanide than Untreated samples (even after blank subtraction); and (5) higher concentrations of sulfide resulted in lower recovery of cyanide.

As shown in Figure 2, hypochlorite had a much stronger effect on cyanide recovery than did sulfide. At the lowest concentration of hypochlorite tested, 3.4×10^{-6} M, cyanide recovery from a 100 ppb CN solution (100 ppb CN, Untreated, 3.4×10^{-6} M Hypochlorite) was approximately 80%. However, at all higher concentrations of hypochlorite tested, the recovery of cyanide was approximately 0% whether the sample was treated with ascorbic acid or not.

Figure 3 shows that for 100 ppb CN, Untreated samples, formaldehyde had little effect on cyanide recovery at the lowest formaldehyde concentration tested (3.7×10^{-7} M), but did substantially reduce recovery of cyanide from 77% to 60% when formaldehyde concentration increased from 3.7×10^{-7} to 3.7×10^{-6} M. Treatment of samples with ethylenediamine was effective in removing the effect of the interference at a formaldehyde concentration of 3.7×10^{-5} M (78% recovery), but not at 3.7×10^{-4} M (10% recovery).

In the case of bisulfite, a threshold response is observed in Figure 4 for the effectiveness of the lead carbonate in removing the effects of bisulfite on cyanide recovery. At 3.2×10^{-5} and 3.2×10^{-4} M bisulfite, cyanide recovery from 100 ppb CN solutions treated with lead carbonate was approximately 45%. At higher concentrations of bisulfite (1.6×10^{-3} and 3.2×10^{-3} M), cyanide recovery was reduced to approximately 11%.

Results for thiocyanate are shown in Figure 5. When the concentration of thiocyanate was increased from 3.9×10^{-7} to 3.9×10^{-5} M, the recovery of cyanide in 100 ppb CN, Untreated samples decreased from approximately 90% to 70%. The high cyanide concentration measured in the blank solution treated with lead carbonate (21 ppb) makes the interpretation of lead carbonate treatment uncertain, but in general, lead carbonate treatment increased the recovery of cyanide relative to untreated samples at the same thiocyanate concentration.

SAMPLE HOLDING TIME

A limited Sample Holding Time Study was also performed prior to the Multiple Interference Study. The sample holding time is the time between sample collection (or preparation of simulated samples) and analysis. If interferences react with cyanide at room temperature or refrigerated temperatures during this period, the final concentration of cyanide determined by the method will not accurately represent the initial cyanide content. Method 335.4 recommends a 14 day sample holding time for cyanide analysis. However, we believed that significant sample alteration could occur within 48 hours, and so conducted a brief study of the effect of holding time on cyanide recovery.

A set of simulated electroplating waste samples was analyzed on the same day they were prepared (Day 0). Half of the samples were analyzed again after one day refrigerated storage (Day 1), and the other half were analyzed after two days refrigerated storage. Percent recovery of the nominal cyanide was calculated for each sample analysis. Selected

results are shown in Table 3. The difference values presented were calculated as the difference between the percent recovery determined on Day 0 and that determined on either Day 1 or Day 2, and are indicators of the stability of the sample over that period. As can be seen in Table 3, the results are highly dependent on the sample composition, and clearly demonstrate that holding time has a large effect on cyanide recovery for some samples.

MULTIPLE INTERFERENCE STUDY

The Multiple Interference Study was a statistically designed study that enabled the estimation of the effects of 6 factors simultaneously on measured cyanide concentrations. Five of the factors were the interference levels, and the sixth factor was the actual cyanide concentration. In addition to statistical aspects, the design also incorporated chemical considerations and results from the Sample Holding Time Study and the Interference Range Finding Studies.

Chemical Aspects of Study Design

The concentrations of cyanide and the five interferences used in the Multiple Interference Study were selected based on three factors that are discussed below: (1) the current regulatory levels for cyanide; (2) the concentrations of interferences that were found to interfere in cyanide analysis in the range finding experiments; and (3) the molar ratios of interferences to cyanide.

Cyanide concentrations were chosen to cover a range of current regulatory discharge levels. For example, discharge to municipal sewer systems requires analysis of cyanide at low concentrations, typically 5-50 ppb CN, while permit levels for electroplating industry discharge are typically around 700 ppb CN. As indicated in Table 4, the study design included cyanide concentrations from 0 to 1000 ppb (0 to 3.8×10^{-5} M). As explained below, the statistical design enabled the best predictions over the range 49 to 500 ppb (1.9×10^{-6} to 1.9×10^{-5} M).

The range of interference concentrations was determined from the results of the preliminary range finding experiments. In general, cyanide recovery was affected by the interference when the interference was at a concentration between 3×10^{-7} M and 3×10^{-4} M. As indicated in Table 4, the range of interference concentrations used in this study was 0 to 1.14×10^{-4} M.

The molar ratio of interference to cyanide was important because the extent of the interference reaction depends on the molar ratio of interference to cyanide as well as on the magnitude of their concentrations. Thus, the study design includes samples with a stoichiometric excess of interferences, a stoichiometric excess of cyanide, and 1:1 stoichiometry of cyanide to interference. The molar ratios of interference:cyanide included in the study ranged from 0.068:1 to 185:1.

Experimental Methods

The results of the Sample Holding Time Study demonstrated the importance of regulating the time between sample preparation and analysis. Thus, each group of samples was prepared and analyzed within a period of approximately 24 hours. On the first day, ten samples (half of a study "block") were prepared, allowed to sit at room temperature for one hour, and then stored refrigerated for approximately 16 hours. On the second day, the samples were brought to room temperature, tested for interferences using the recommended spot tests, and those in which interferences were detected were treated using the recommended interference removal method. Then all ten samples were distilled and analyzed. The same process was then repeated for the second half of the study "block."

Statistical Study Design

The statistical study design consisted of 120 samples (trials) arranged in six blocks of 20. Each block had 18 samples containing cyanide and two blank samples. Of the 72 non-blank samples in blocks 1 through 4, 64 samples contained cyanide (factor Z_1 ; Table 4) at either 49 or 500 ppb, and each of the interferences (factors Z_2 , Z_3 , Z_4 , Z_5 , and Z_6 ; Table 4) at either 0 or 1.14×10^{-4} M. These 64 trials represent a complete 2^6 factorial arrangement (i.e., all possible combinations of high and low levels of each of six factors). In addition to the 64 factorial points and the blanks, each of the first four blocks also contained two "center points," with cyanide concentration of 160 ppb and interference concentration of 1.07×10^{-6} M for all five interferences. When the mathematical transformation used in this study (i.e., a logarithmic transformation) is applied to these concentrations, the "center points" fall near the center of the factorial design (i.e., about half way between the low and high levels of each factor). Blocks 5 and 6 each consisted of three center points, 6 pairs of points in which each factor was varied about the center point one factor at a time, and three points chosen to examine stoichiometric relationships.

Two deviations from the experimental design were performed. First, the actual concentration of interferences in some of the block 5 and 6 samples was 2.6×10^{-6} M rather than 1.07×10^{-6} M. Second, an additional block of samples was prepared and analyzed. The extra block was a re-run of block 1 with the exception that samples were analyzed immediately after preparation, rather than 24 to 48 hours later. The effect of this difference on the final model was negligible, so the additional samples were included in the data analysis.

Statistical Analysis

The goal of the statistical analysis was to characterize how measured cyanide concentrations were affected by actual cyanide concentrations and by the concentrations of one or more of the interferences. After considering a number of candidate model forms, we selected the following class of models for detailed analysis:

$$\ln[Y+1] = \ln[1+A+BZ_1] + \epsilon$$

where Y denotes the measured cyanide concentration, Z_1 is the KCN concentration, ϵ is a random error term, and A and B are functions of the interferences having the form:

$$A = B_0 + f_1(Z_2, Z_3, Z_4, Z_5, Z_6)$$

$$B = B_1 + f_2(Z_2, Z_3, Z_4, Z_5, Z_6)$$

where B_0 and B_1 are constants and f_1 and f_2 are polynomial functions of the interference concentrations that are zero when none of the interferences are present. The model allows each interference (a) to have an additive effect (i.e., to change the intercept) with the incremental amount being proportional to its concentration; (b) to have a multiplicative effect (i.e., to change the slope) with the increment being proportional to its concentration; and (c) to have both effects (a) and (b). In addition, the interferences are allowed to interact with one another (e.g., by including cross-product terms in the f_1 and f_2 functions) and thereby jointly affect either A or B or both.

Thus the objectives of the statistical analysis were first to determine "good" forms for the A and B functions and then to estimate the parameters of those functions. Nonlinear least squares estimations were performed using the SAS NLIN procedure.

Results

Statistical analysis of the data resulted in the following representations for A and B:

$$A = B_0 + B_2Z_2 + B_3Z_3 + B_4Z_4 + B_5Z_5 + B_6Z_6 + B_{22}Z_2^2 + B_{33}Z_3^2 + B_{55}Z_5^2 + B_{24}Z_2Z_4 + B_{36}Z_3Z_6 + B_{45}Z_4Z_5$$

and

$$B = B_1 + B_{12}Z_2 + B_{13}Z_3 + B_{14}Z_4 + B_{15}Z_5 + B_{16}Z_6 + B_{123}Z_2Z_3 + B_{133}Z_3^2$$

Thus the final model is given by:

$$\begin{aligned}
\text{Predicted [CM]} = & \\
& B_0 + B_1 [\text{CM}] + B_2 [\text{S}] + B_3 [\text{OCI}] + B_4 [\text{HCHO}] + B_5 [\text{HSO}_3] + B_6 [\text{SCN}] \\
& + B_{12} [\text{CM}] [\text{S}] + B_{13} [\text{CM}] [\text{OCI}] + B_{14} [\text{CM}] [\text{HCHO}] + B_{15} [\text{CM}] [\text{HSO}_3] + B_{16} [\text{CM}] [\text{S}] \\
& + B_{22} [\text{S}]^2 + B_{33} [\text{OCI}]^2 + B_{55} [\text{HSO}_3]^2 \\
& + B_{24} [\text{S}] [\text{HCHO}] + B_{36} [\text{OCI}] [\text{SCN}] + B_{45} [\text{HCHO}] [\text{HSO}_3] \\
& + B_{123} [\text{CM}] [\text{S}] [\text{OCI}] + B_{133} [\text{CM}] [\text{OCI}]^2
\end{aligned}$$

The estimated parameters are given in Table 5, along with an estimate of their standard errors and approximate 95 percent confidence intervals. Asterisks are used to identify those coefficients which are statistically significant. The model results are presented in 3-dimensional graphs in Figures 6 to 11, with each graph presenting the predicted percent recovery of cyanide as a function of the actual KCN concentration and the concentration of one interference. The other interferences are held at a concentration of 0 for these simulations, except where noted.

As can be seen in Figure 6, increasing the concentration of sulfide results in decreasing the percent recovery of cyanide. The effect is most dramatic at low concentrations of KCN, and less so as the concentration of KCN increases. This general pattern is repeated to a lesser extent for bisulfite (Figure 7), formaldehyde (Figure 8), and thiocyanate (Figure 9). In the case of hypochlorite (Figure 10), the effect of increasing the hypochlorite concentration is a highly significant decrease in predicted percent recovery of cyanide, such that at the highest concentrations of hypochlorite and cyanide included, the predicted percent recovery approaches 0.

One effect that was not originally anticipated was the combined effect of hypochlorite and thiocyanate. As illustrated in Figure 11, for a fixed concentration of hypochlorite (0.1 mM) and variable concentration of thiocyanate, the predicted percent recovery of cyanide ranges from approximately 0 to 1000%. The explanation for this pattern is that, at low concentrations of thiocyanate, hypochlorite rapidly oxidizes cyanide to carbon dioxide and thus very little cyanide is present at the time of the analysis. At high concentrations of thiocyanate, hypochlorite oxidizes thiocyanate to sulfate plus cyanide, and thus increases the concentration of cyanide prior to analysis. Thus, the actual concentration of cyanide present at the time of analysis depends on the ratios of hypochlorite to thiocyanate and hypochlorite to KCN as well as the ratio of thiocyanate to KCN.

During the Multiple Interference Study, we tested each sample for the presence of each interference using the recommended interference recognition tests. The results are summarized in Table 6 and show that the interference recognition tests failed to correctly identify the presence of sulfide, hypochlorite, or formaldehyde in over half of the samples containing those interferences. In general, the presence of more than one interference caused each of the interferences to be "masked" during interference recognition testing.

CONCLUSIONS

Several conclusions were drawn from these studies:

1. As demonstrated in the Interference Range Finder Studies, individual interferences caused a substantial reduction in recovery of cyanide in some cases, even after application of the interference removal method.

2. Sample holding time was an important parameter that lead to an increase or a decrease in cyanide recovery as a function of time. The effect was a function not only of the interferences present in the sample, but also of the concentration of each interference and the length of time the sample was held. The fact that significant sample alteration was observed within 48 hours suggests that the 14 day holding time recommended in Table II of Method 335.4 and 40 CFR Part 136.3 is excessive.

3. In the Multiple Interference Study, it was observed that the interference recognition tests worked properly in less than 50% of the samples when multiple interferences were present.

4. The effect of the interferences on cyanide and on each other was complex. Not only was the effect of each interference on cyanide recovery statistically significant, but there were also statistically significant 2-way interactions between sulfide and formaldehyde, hypochlorite and thiocyanate, and formaldehyde and bisulfite, and a statistically significant 3-way interaction among cyanide, sulfide, and hypochlorite.

5. Hypochlorite was not considered a method interference by itself. It caused a rapid removal of cyanide prior to analysis, but if the excess hypochlorite was adequately removed in the pretreatment stage, then the method did accurately determine the concentration of cyanide present at the start of the analysis. However, in the presence of other oxidizable interferences, such as thiocyanate, sulfide, or formaldehyde, the effect of hypochlorite was more complex and time dependent, and the method did not provide reproducible or reliable results.

6. The word "Total" in the Total Cyanide Methods may be interpreted absolutely and lead to improper treatment of cyanide wastewater. Clearly the word "Total" is not representative of the results produced by these cyanide methods when multiple interferences are present and/or when interferences are not identified and removed.

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QUESTION AND ANSWER SESSION

MR. LOEWE: Jeff Loewe with Daily Analytical Labs. Is the holding time before or after the distillation?

MS. GOLDBERG: It is before the distillation.

MR. LOEWE: Were the samples held after distillation?

MS. GOLDBERG: No, we did not. We always analyzed the samples the same days that they were distilled.

MR. LOEWE: Okay, thank you.

MR. JOHNSON: Mike Johnson with Dupont. I am one of the poor people in the regulated community that has to use this method, and I applaud you, because you have found exactly what we have found.

The question is right now, that method is the only method EPA has approved for cyanide, and what we are seeing is negative values which I do not mind as long as EPA lets us use it in our average, but that is another topic. We are seeing positive interferences. It is just all over the map.

Is there any recommendation on another method? We have been experimenting with the weak acid dissociable test and getting a lot better results from that. It seems to be ignoring a lot of the interferences, but from a regional standpoint, they do not recognize that as a method. So, what is somebody to do?

MS. GOLDBERG: I think we will have two responses to that. I will tell you my answer, and then I will ask Bill Potter to speak for EPA.

The first answer is that we are working on method improvements to this, and we have actually seen some improvements by using weaker oxidants than the hypochlorite.

The goal there is to oxidatively decompose the interferent but not oxidize the cyanide, and we have had very good success adding sodium vanadate as an interferent removal oxidant. It does not work with the thiocyanate. So, it will remove the other interferences for you but not the thiocyanate. For that, we have no recommendation.

We are currently exploring other methods, and I cannot give you any results from those yet. One of the studies we have not even started yet, and others are just in the process, so I cannot give you that recommendation, but maybe Bill can tell you some more.

MR. TELLIARD: Bill?

MR. POTTER: In response to coming up with different methods, right now, we are not funded for looking or exploring other methods. This particular project was designed only to find out if the classical method could be improved or if the interferences could be identified and handled in some way.

What this study has shown is that the method is dysfunctionate as written.

MR. TELLIARD: If you have a suggestion as to a method or an application, if you would send it to me, I would do what I can to get it addressed. No promises, but we are certainly interested, in the industrial industries that we regulate and are writing regulations for; we have to have a method. I have been waiting for this paper all day.

MR. TELLIARD: Thank you. The gentleman in the back?

MR. STRAKA: My name is Mike Straka, and I am with Perstorp Analytical Environmental. A couple of comments. First of all, I am very glad to hear that response to the request for better methods. We, as an instrumentation manufacturing company, are devoting a lot of energy to this specific problem, that is, the cyanide problem.

We have, in cooperation with the University of Nevada-Reno Mackey School of Mines, begun to commercialize a new weak acid dissociable chemistry that precludes the need to do a distillation and, therein, cures a lot of ills and evils.

The distillation plus colorimetric finish can take up to an hour or more, more like an hour and a half per sample. With this new method, we can get results identical to a distillation followed by ion chromatography finish in two minutes per analysis, and I promise you the interferences are what you would expect.

So, my question actually to Bill is I have the method that you are looking for. Now, tell me how I can get it through the EPA or get it evaluated rapidly.

MR. TELLIARD: We would be glad to take a look at it.

MR. STRAKA: Anything that I can do to help, I would appreciate it.

MR. TELLIARD: I understand.

MR. STRAKA: One comment, actually, to Margaret. Is it really fair to classify bisulfite and hypochlorite and those other oxidizers as interferences? As you mentioned, they are clearly oxidizing the cyanide, and they would only be expected to be in the sample because someone is trying to actually destroy the cyanide before it becomes an effluent.

MS. GOLDBERG: Well, in the case of the hypochlorite, that is true. The hypochlorite is added to remove the cyanide to enable discharge, and that was, I think, the comment that I made at the end, that it is not really considered an interference in itself, because it really is removing the cyanide.

The difficulty with the hypochlorite is that it is also oxidizing the other interferences present and that there are very complicated reaction pathways proceeding. It makes it very difficult to regulate on a method where you can get between zero and 1000 percent recovery.

So, I think, in that sense, we do have to consider the interactions of the hypochlorite with the other interferences as method interferences.

The bisulfite itself is not added as an oxidant deliberately to remove the cyanide, typically. Usually, that is present as a brightener or other component by the electroplaters. So, that is in the sample and is not added as an oxidant.

MR. STRAKA: In some industries, it actually is, but my final comment, and I will let you go, is it has been our observation that by adding lead sulfide to the acceptor or the scrubber solution that we can have some interesting chemical kinetics going on there, too, which catalyze the cyanide and actually produce thiocyanate which may be a mechanism for giving rise to your lower recovery in the total procedure. That is to say that the sulfide plus cyanide yields thiocyanate.

I just make that general observation, because I know a lot of people traditionally do that for the total distillation, whereas if you do an amenable or WAD distillation, they do not use that practice, and sometimes, more often than not, you can end up getting WAD cyanide results that are higher than your totals, and that may be a very real mechanism for that interference.

Thank you.

MS. GOLDBERG: You are right. Thank you.

MR. TELLIARD: Thank you.

MR. SAWYER: My name is Bernard Sawyer. I am with the Metropolitan Water Reclamation District of Chicago. We have done a lot of work

on cyanide analysis using a UV lamp with the thin film distillation, and it breaks down the thiocyanate. That method is approved in the ASTM manual, and it was sent in at one point or another to EPA, but it never made it, for whatever reason, as being an approved EPA method, but we have used it for many years, especially on industrial waste samples.

It seems to eliminate a lot of these interferences, and it totally eliminates your thiocyanate problem, because you actually run the analysis twice. It is done on a Technicon train, and you basically have the UV lamp turned on, and then you turn the lamp off, and the difference in the two gives you your thiocyanate value which you then can subtract out.

A lot of work has been done with that at our labs, I know, to show the percent recoveries of all the different thiocyanate complexes, et cetera, and it has been published in the Water Pollution Control Federation Journal from many years ago.

So, there is some information out there.

MR. TELLIARD: Yes. The other thing is that, of course, there is a rule in ASTM that no method can go final while the author is alive.

MR. POTTER: Let me say something about that. That was, I believe, Nebi Kelada's method, and the purpose of this particular paper was just to look at the method that was already approved. So, we are now, since we have completed this experimentation, starting to look at Kelada's method, along with many other techniques, some of them UV techniques. There are membrane separation techniques.

With the remaining amount of money that we have in the contract, we may be able to review some of those on a very cursory sort of a quick look or snapshot.

MR. TELLIARD: Thanks, Bill.

MR. XIE: Jack Xie from Water Chemistry in Roanoke, Virginia. My question is I have percent recovery from zero percent here to 1000 percent. How do you record for your QA/QC data? Because some EPA methods require that the percent recovery should fall into a certain range, like 60 percent to 120 percent, but when you have a situation when your percent recovery is from zero to 1000, how do you deal with that?

MS. GOLDBERG: Well, I think, as Bill has said, the fact that we had 1000 percent recovery really is just showing that the method is dysfunctional. There is no way to show that those are good values. In fact, they are fairly non-reproducible. We can get 1000 percent recovery today, and we can get 1200 percent recovery tomorrow.

I did not speak at all about the quality control activities that we used in this lab. We have used a lot of procedures to establish our quality control levels.

Each day that we ran the cyanide distillation blocks with ten samples in them, we also ran a whole quality control block which contained four blanks plus four cyanide samples dosed at 100 ppb. Half of each of those groups were with the lead carbonate and the other half without, so that we tracked on a daily basis the performance of our entire process.

We kept quality control charts for that and for undistilled KCN just on a colorimetric analyzer as well so that we were able to distinguish on a daily basis if there were any problems with the distillation block or if there were any problems with the colorimetric analysis.

We felt that the quality control was well under control for that study and the observed 1000 percent recovery really were oxidative effects of the interferences.

MR. XIE: Okay, thanks.

MR. TELLIARD: Thank you. Thanks, Margaret.

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TABLE 1. POTENTIAL INTERFERENCES IN ELECTROPLATING INDUSTRY WASTE

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- Sulfide (S^{2-})
 - Thiocyanate (SCN^-)
 - Carbonates (HCO_3^- , CO_3^{2-})
 - Nitrite (NO_2^-)
 - Oxidants (ClO_4^- , O_3 , H_2O_2)
 - Bisulfite (HSO_3^-)
 - Formaldehyde (HCHO)
 - Surfactants
 - Metals
-

TABLE 2. ELECTROPLATING INTERFERENCES STUDIED

INTERFERENCE	SPOT TEST	REMOVAL METHOD
Sulfide	Yes	PbCO ₃
Hypochlorite	Yes	Ascorbic Acid
Formaldehyde	Yes	Ethylenediamine
Thiocyanate	No	None (PbCO ₃)
Bisulfite	No	None (PbCO ₃)

TABLE 3. HOLDING TIME STUDY

SAMPLE	SAMPLE COMPOSITION (10 ⁶ M)							PERCENT RECOVERY (%)			
	CN	S	OCI	HCHO	HSO ₃	SCN	DAY 0	DAY 1	DAY 2	DIFFERENCE (%)	
A	1.9	0	0	0	114	114	79		72	-7	
B	1.9	0	114	114	0	0	40	29		-11	
C	1.9	0	114	114	114	114	989		1101	+112	
D	1.9	114	0	114	0	114	83		56	-27	
E	1.9	114	0	114	114	0	78	90		+13	
F	1.9	114	114	0	0	114	56	1089		+1033	
G	19.2	0	0	114	0	114	71	75		+4	
H	19.2	0	114	0	0	114	122	95		-26	
I	19.2	0	114	0	114	0	4.0		2.8	-1.2	
J	19.2	114	0	0	0	0	59	69		+10	
K	19.2	114	0	0	114	114	59		70	+11	
L	19.2	114	114	114	0	0	32	40		+8	
M	19.2	114	114	114	114	114	78	146		+68	
N	6.15	1.07	1.07	1.07	1.07	1.07	91		64	-27	
O	6.15	1.07	1.07	1.07	1.07	1.07	90		58	-32	

TABLE 4. STUDY DESIGN

CHEMICAL	FACTOR	CONCENTRATION RANGES	
		DESIGN	PREDICTION
KCN	Z ₁	0-1000 µg/L (ppb)	49-500 µg/L (ppb)
Sulfide	Z ₂	0 - 1.14 x 10 ⁻³ M	0 - 1.14 x 10 ⁻⁴ M
Hypochlorite	Z ₃	0 - 1.14 x 10 ⁻³ M	0 - 1.14 x 10 ⁻⁴ M
Formaldehyde	Z ₄	0 - 1.14 x 10 ⁻³ M	0 - 1.14 x 10 ⁻⁴ M
Bisulfite	Z ₅	0 - 1.14 x 10 ⁻³ M	0 - 1.14 x 10 ⁻⁴ M
Thiocyanate	Z ₆	0 - 1.14 x 10 ⁻³ M	0 - 1.14 x 10 ⁻⁴ M

TABLE 5. ESTIMATED MODEL PARAMETERS

PARAMETER ESTIMATE	ASYMPTOTIC STD. ERROR	95% CONFIDENCE INTERVAL	
		LOWER	UPPER
B0 1.21697E+01***	9.28269E-01	1.03311E+01	1.40082E+01
B1 6.72741E-01***	2.82236E-02	6.16841E-01	7.28642E-01
B2 -1.56419E-03***	3.01774E-04	-2.16189E-03	-9.66490E-04
B3 9.26762E-04***	2.62156E-04	4.07529E-04	1.44600E-03
B4 -5.13696E-04***	1.80544E-04	-8.71286E-04	-1.56107E-04
B5 -8.85959E-04***	2.70073E-04	-1.42087E-03	-3.51046E-04
B6 -6.20955E-04*	3.53309E-04	-1.32073E-03	7.88193E-05
B22 9.85605E-09***	3.57131E-09	2.78263E-09	1.69295E-08
B33 -1.82170E-08***	2.44597E-09	-2.30615E-08	-1.33724E-08
B55 5.80259E-09**	2.71985E-09	4.15579E-10	1.11896E-08
B12 -5.79119E-07	1.81319E-06	-4.17036E-06	3.01212E-06
B13 -6.50880E-05***	2.93706E-06	-7.09053E-05	-5.92708E-05
B14 -9.21116E-07	9.47768E-07	-2.79829E-06	9.56058E-07
B15 1.13738E-06	8.57594E-07	-5.61196E-07	2.83595E-06
B16 6.67081E-07	2.67670E-06	-4.63447E-06	5.96863E-06
B24 8.09171E-08**	3.34711E-08	1.46234E-08	1.47211E-07
B36 4.48756E-06***	3.09200E-07	3.87515E-06	5.09997E-06
B45 7.55712E-08***	2.58539E-08	2.43644E-08	1.26778E-07
B123 3.27211E-09***	3.78161E-10	2.52312E-09	4.02111E-09
B133 5.11637E-10***	2.36651E-11	4.64766E-10	5.58509E-10

TABLE 6. INTERFERENCE RECOGNITION TESTS

	INTERFERENCE		
	S ²⁻	OCI ⁻	HCHO
Number of Interference-Containing Samples Tested	57	57	57
Number Correctly Identified	2	9	24
Percent Correctly Identified	4%	16%	42%

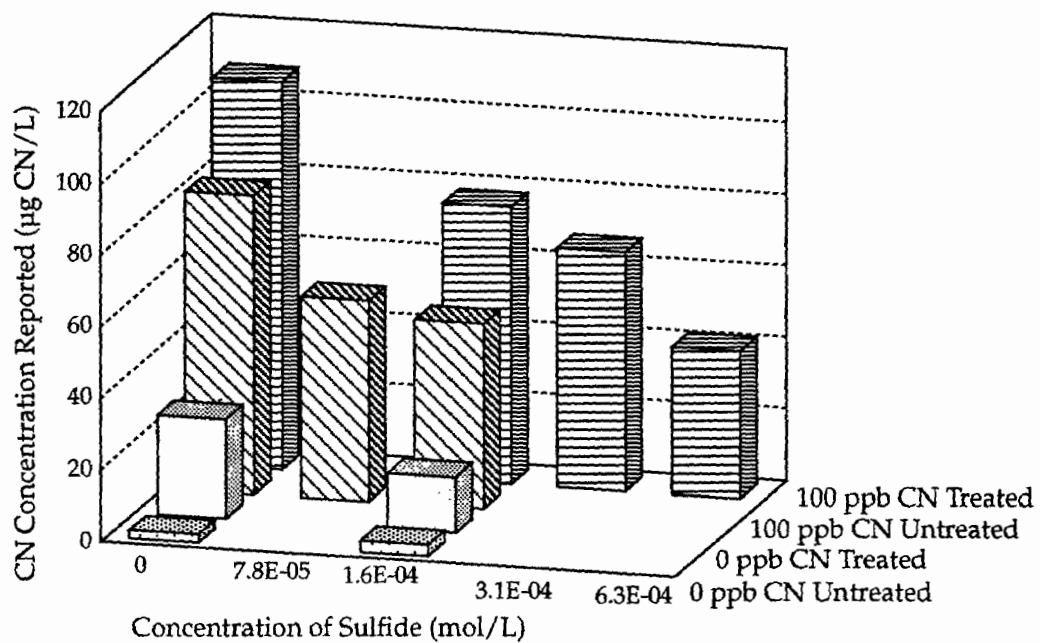


Figure 1. Sulfide: Treated samples contain PbCO_3 in the Absorber Tube.

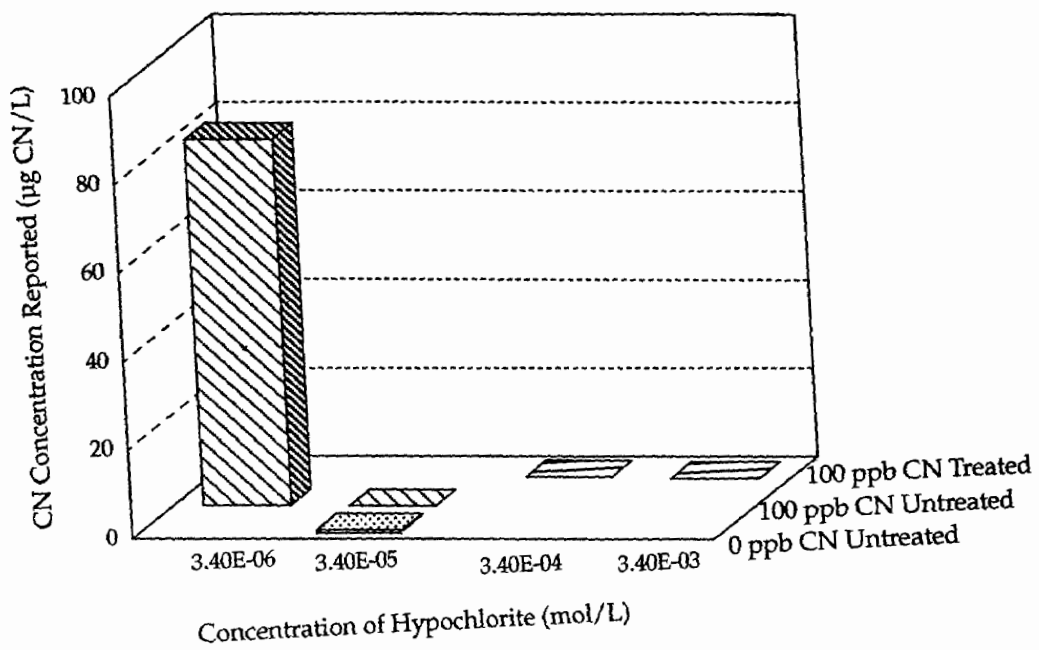


Figure 2. Hypochlorite: Treated samples contain Ascorbic Acid.

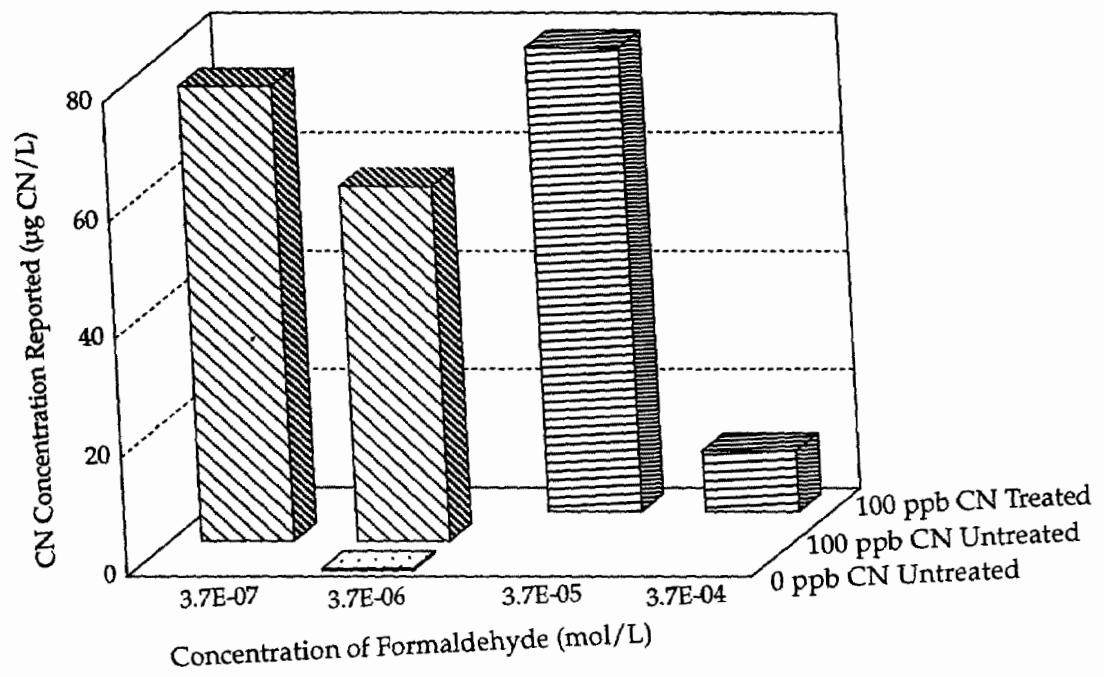


Figure 3. Formaldehyde: Treated samples contain Ethylenediamine.

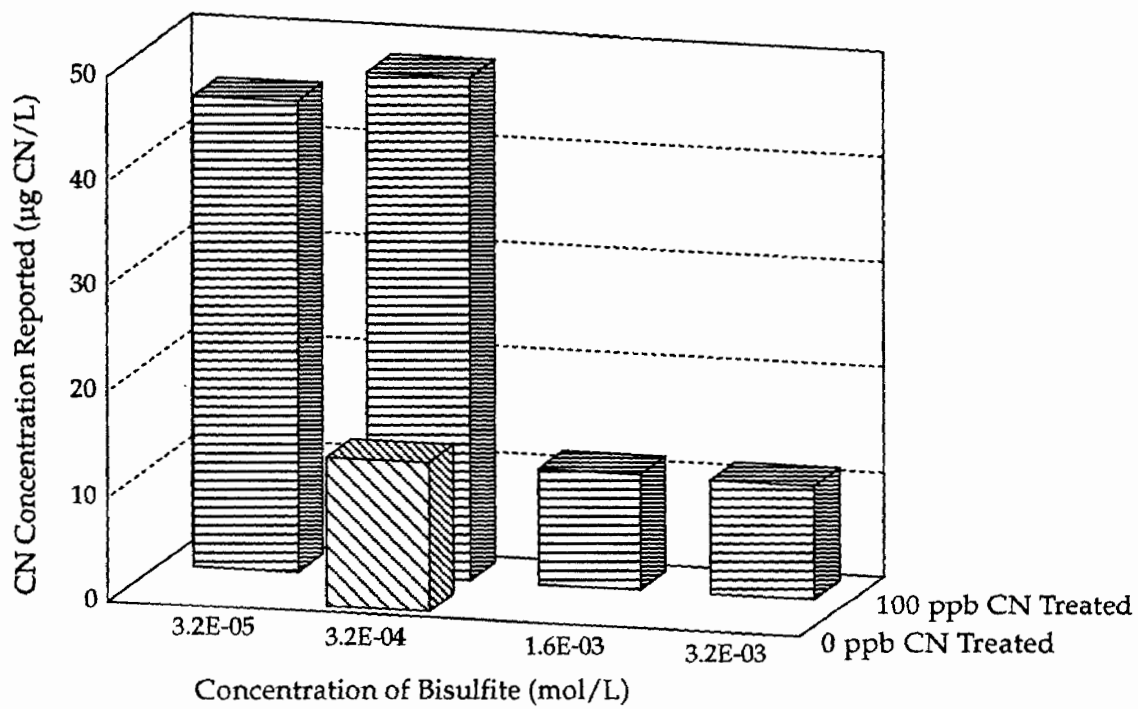


Figure 4. Bisulfite: All samples treated with PbCO_3 in each Absorber Tube.

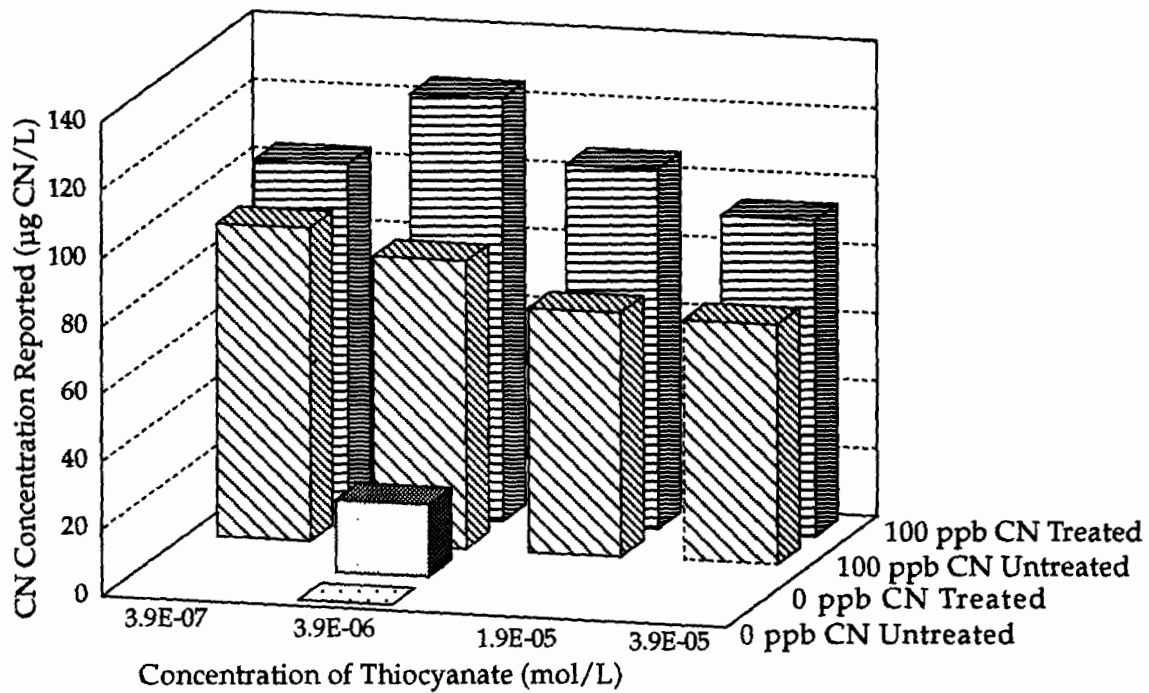


Figure 5. Thiocyanate: Treated samples contain $PbCO_3$ in the Absorber Tube.

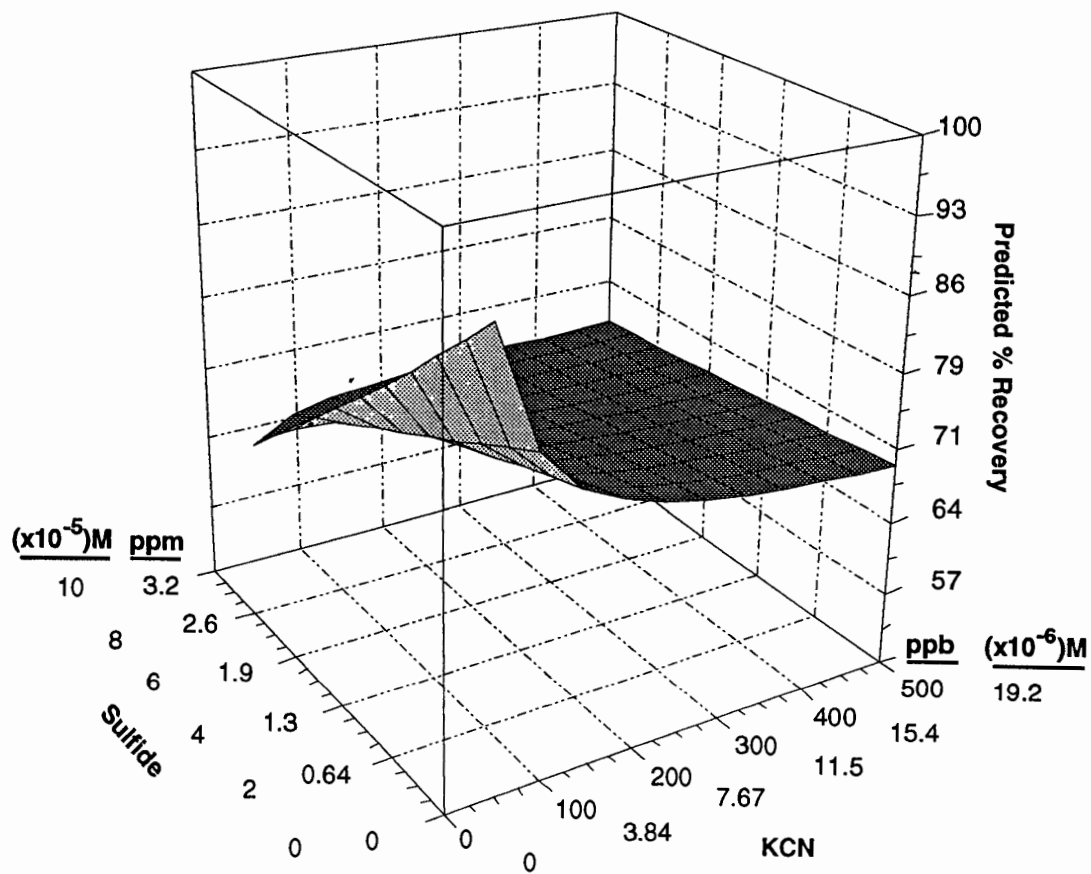


Figure 6. Sulfide: Predicted cyanide recovery.

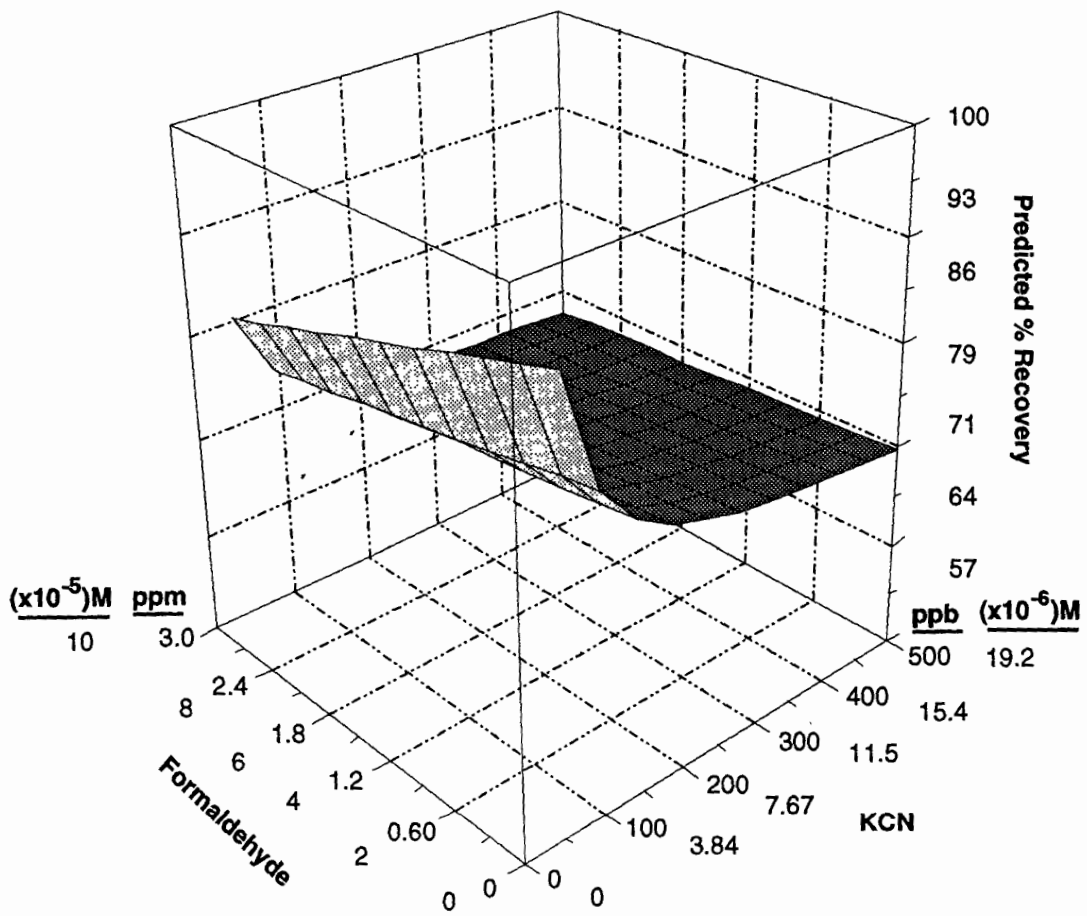


Figure 7. Formaldehyde: Predicted cyanide recovery.

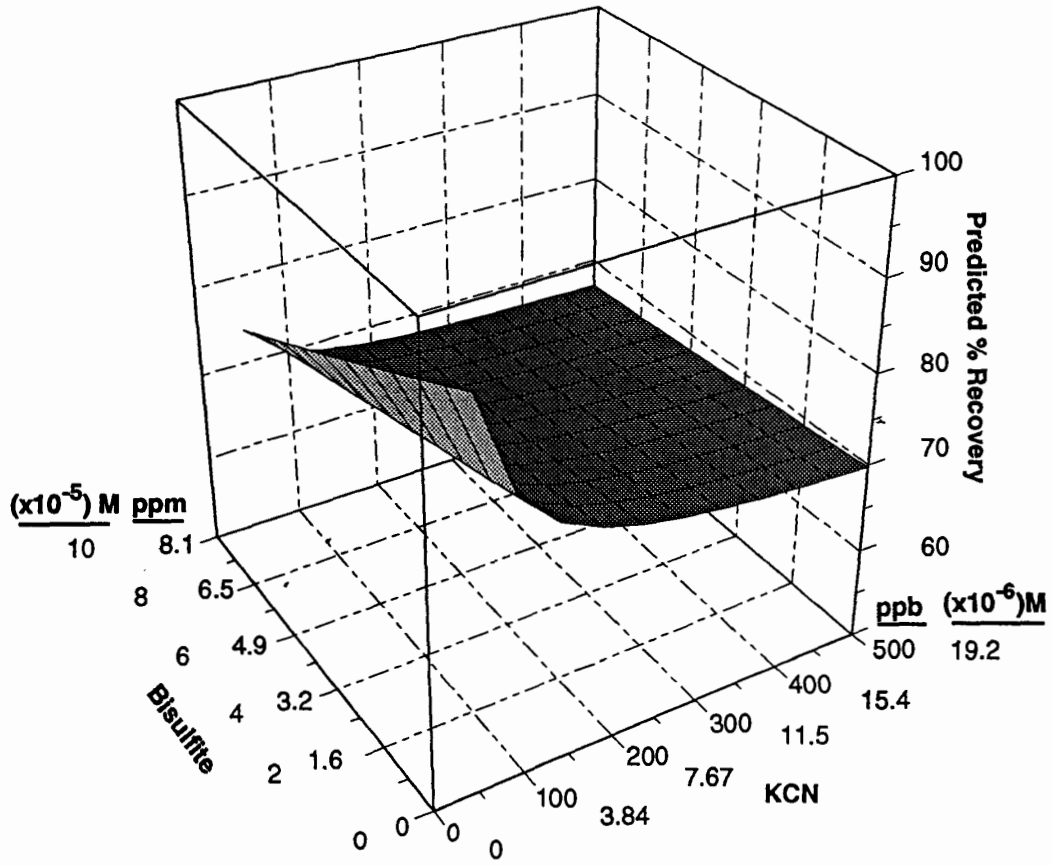


Figure 8. Bisulfite: Predicted cyanide recovery.

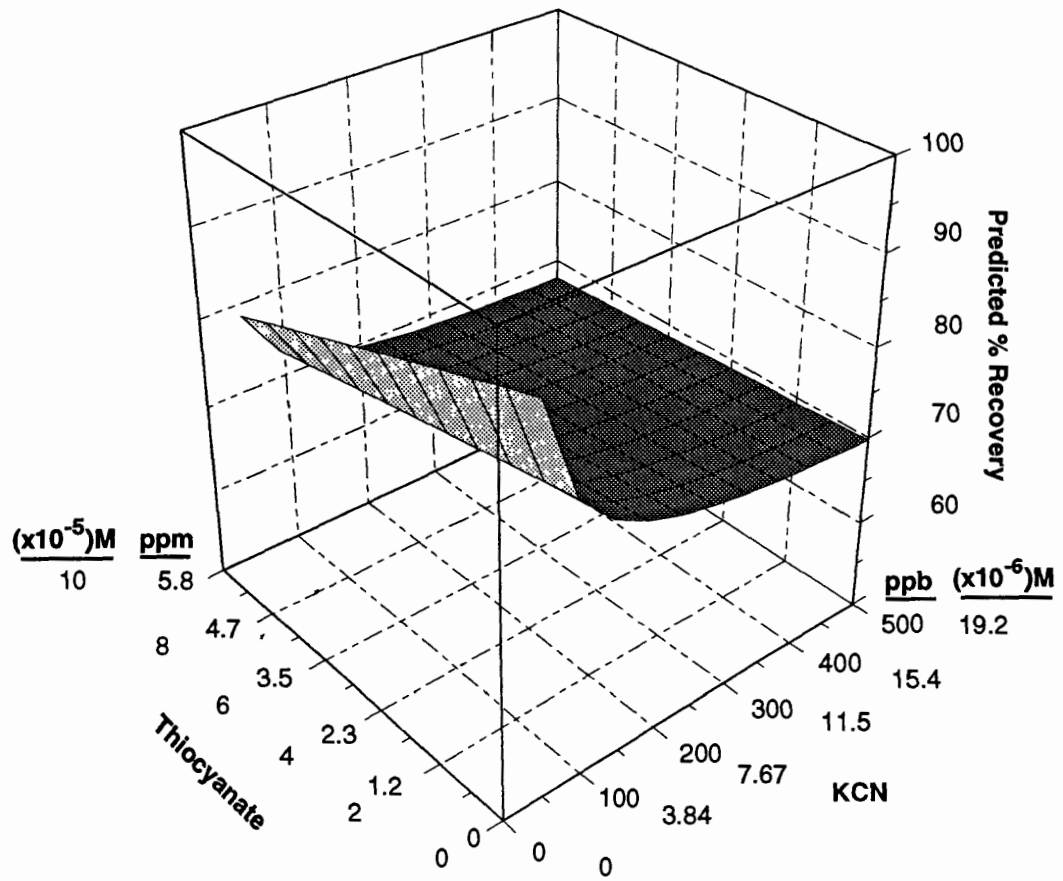


Figure 9. Thiocyanate: Predicted cyanide recovery.

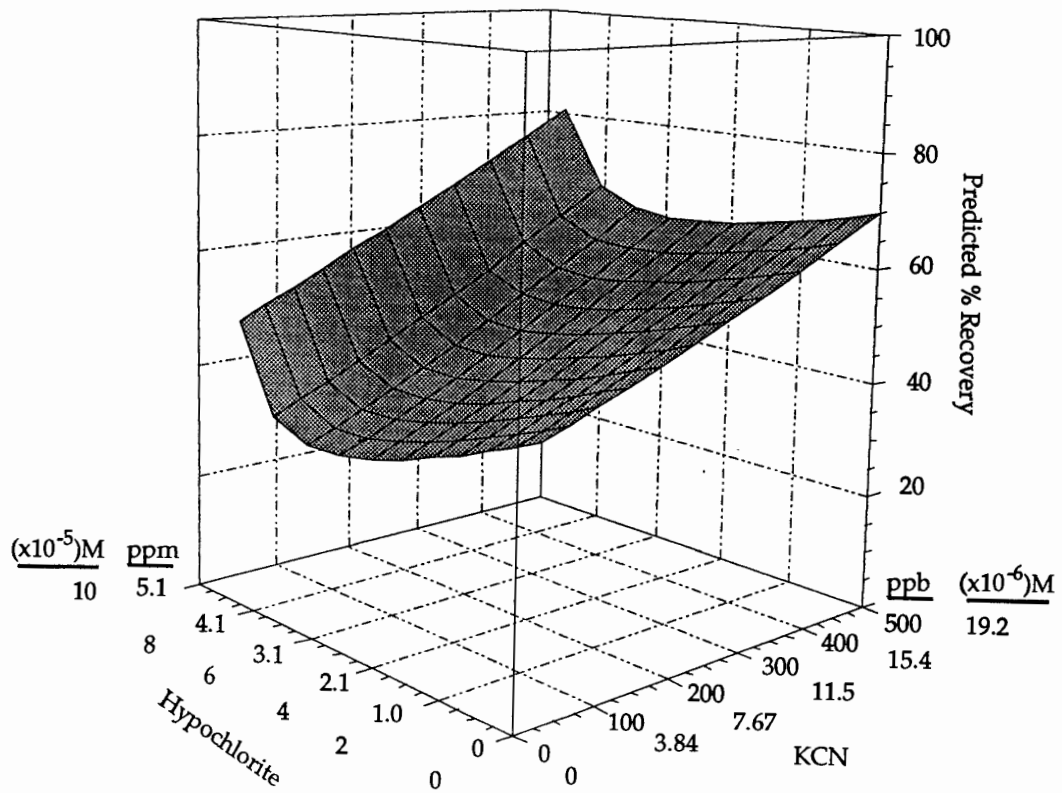


Figure 10. Hypochlorite: Predicted cyanide recovery.

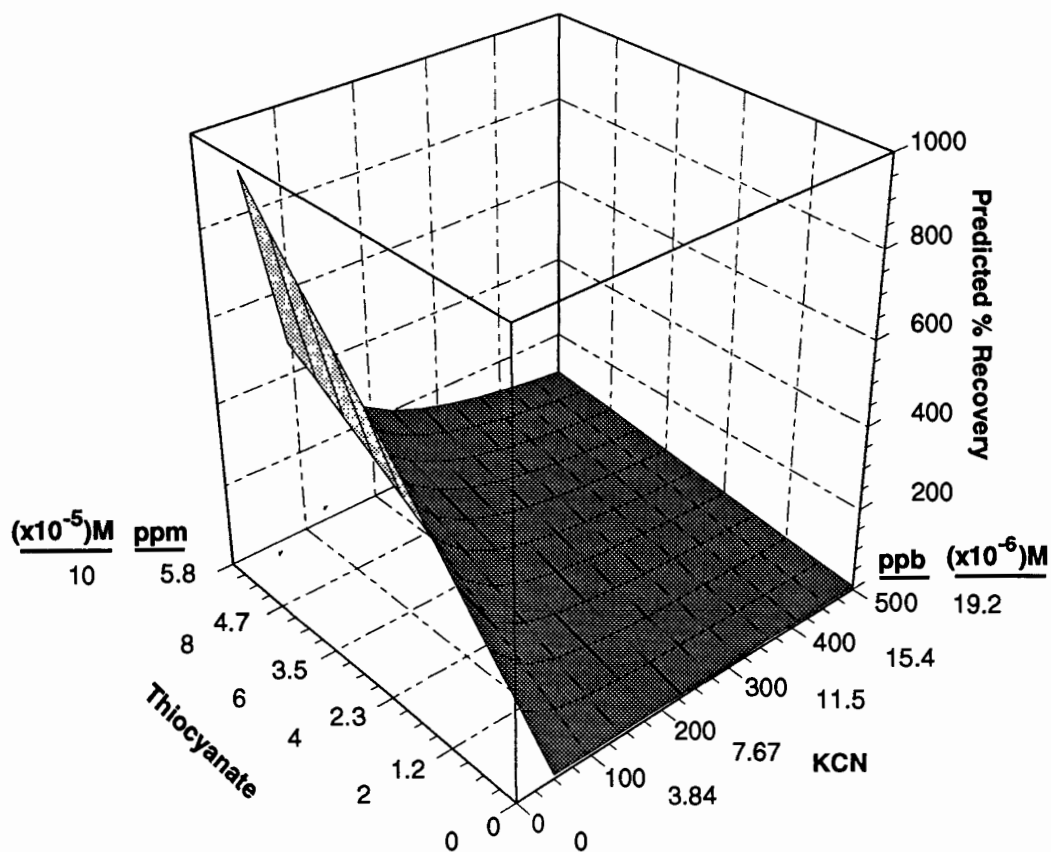


Figure 11. Thiocyanate with 0.1 mM hypochlorite: Predicted cyanide recovery.