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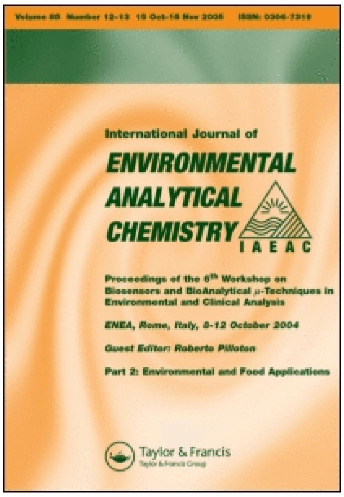

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DETERMINATION OF FREE CYANIDE IN SOUR WATER AT FLUID CATALYTIC CRACKING (FCC) PLANTS

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An analytical method has been developed to analyze free cyanide in FCC sour water containing high concentration of H_2S. In this method, the cyanide is first converted into thiocyanate by reacting with H_2S and hydrogen peroxide and then the concentration of thiocyanate is measured by ion-chromatography. Because H_2S in the sour water acts as a co-reactant in the conversion of cyanide, pretreatment for preventing the interference by H_2S is not required, and the thiocyanate and free cyanide can each be measured precisely and accurately.

The optimum reaction conditions including pH, H_2O_2/H_2S molar ratio and reaction time were examined. The interference from some specific foreign ions and unknown species in the field samples were also investigated. This analytical technique has been successfully applied in the HCN measurement of field samples. The detection limit for the free cyanide is 9 μg/L and the standard error is ± 2%.

Keywords: Cyanide analysis; sour water

INTRODUCTION

The sour water produced from Fluid Catalytic Cracking (FCC) plants in a refinery often contains 5–50 mg/L of HCN. HCN is the cause for corrosion.[1,2] To prevent corrosion and resulting plugging in piping and equipment, a corrosion inhibitor is required. The dosage of a corrosion inhibitor such as polysulfide is based on the quantity of HCN, and thus it becomes crucial to accurately determine the HCN concentration in the sour water.

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A concentration of about 2 g/L of H_2S is commonly present in the sour water. This causes a severe interference in the HCN measurement. Generally, a pretreatment which removes H_2S by reacting the sour water with $PbCO_3$ or $Pb(CH_3COO)_2$ is required. However, such a pretreatment step costs time and occasionally results in unacceptable error.[3,4]

Thiocyanate is stable and easy to measure by spectrophotometric method. Miura et al.[5,6] developed an analytical procedure for converting sulfide and cyanide to thiocyanate, and forming a complex compound with ferric ion. The complex was then measured spectrophotometrically and the detection limit of this method was reported to be 10^{-5} M.

Another method developed by Koh et al.[7,8] was composed of extracting thiocynate by using methylene blue-containing solvent and measuring the extract spectrophotometrically. The detection limit of this method was 10^{-6} M. However, high concentration of H_2S still causes serious interference problem in the above mentioned methods. Therefore a new method without such an interference problem should be developed.

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In the present study, we propose an analytical method in which the H_2S in sour water acts as a co-reactant, thus its interference on the analysis of cyanide is avoided. In this proposed method, the cyanide is first converted to thiocyanate by reacting with H_2S and H_2O_2:

$$H_2S + HCN + H_2O_2 \rightarrow HSCN + 2\ H_2O \qquad (1)$$

and then the concentration of HSCN is measured by ion-chromatograghy (IC) with a conductivity detector directly. The detection limit of this method is 10^{-6} M. Note that the pretreatment of removing H_2S is not needed because H_2S is a co-reactant in the conversion of cyanide.

The objective of this study is to introduce this new method and to find an optimal reaction condition for converting cyanide to thiocyanate through equation (1).

EXPERIMENTAL

Chemicals and apparatus

All chemicals used were of analytical-reagent grade and were used without further purification. Doubly distilled water was used in all experiments. A cyanide solution was prepared by dissolving 3.5 g of potassium cyanide in 250 mL of sodium hydroxide solution (40 g/L) and was standardized with a silver nitrate solution.[9] Working standard cyanide solutions were prepared by suitable dilution with water.

The sulfide solution used for converting the cyanide was prepared by absorbing H_2S gas with a 1 N sodium hydroxide solution, and was standardized with a silver nitrate solution, and adjusted to about 0.313 M with a 1 N sodium hydroxide solution. This solution was stored in a refrigerator and consumed used within one week.

A thiocyanate solution (about 0.1 M), which was standardized against silver(I) solution by the Volhard's method,[10] was employed to prepare working standards by suitable dilution with water. The working standards were used to ascertain the stoichiometric formation of thiocyanate from cyanide. Borax buffers (0.025 M), disodium hydrogen phosphate buffer (0.05 M) and various amounts of sodium hydroxide were used to adjust the pH of the solution for the formation of thiocyanate from cyanide. Hydrogen peroxide solution of 35 wt% purchased from Merck Co. was standardized by iodometry, and working solutions were prepared by suitable dilution.

A Dionex Model DX500 Ion-chromatography (IC) system was employed for all measurements. The basic hardware comprised a Dionex AS-11 4 mm column, Dionex GP40 pump, Dionex CD20 conductivity detector, and an auto-sampling system Tsp Model AS-3500. A 0.025 N sodium hydroxide solution was used as mobile phase. The injection volume of the sample varied from 10 μL to 100 μL.

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Analytical

First, the existing sulfide concentration of samples was determined by silver nitrate solution, and the existing thiocyanate in the sample was quantified by IC without any pretreatment. Then, the cyanide content was determined by converting cyanide into thiocynate and measured by IC.

If the existing sulfide concentration is below 0.03 M, then additional sulfide should be supplemented and Procedure I followed. Otherwise, Procedure II should be implemented.

Procedure I: low sulfide samples

One milliliter of 0.313 M sulfide solution and 10 mL of the sample solution containing up to 10^{-4} M cyanide were poured into a 20 mL glass vial. This mixture was well mixed by an electromagnetic stirrer and then 1 mL of 0.62 M hydrogen peroxide solution was added. After the mixture (pH 11–12) being allowed to react for 40 min, the thiocyanate content was measured by IC.

The amount of thiocyanate converted from cyanide was obtained by the difference between sulfide-treated and non-treated samples. Thus, both thiocyanate and cyanide contents were determined.

Procedure II : high sulfide or FCC sour water samples

One milliliter of 0.1 N sodium hydroxide solution and 10 mL of the sample solution containing up to 10^{-4} M cyanide were poured into a 20 mL glass vial. This solution was well mixed by an electromagnetic stirrer with addition of 1 mL of hydrogen peroxide solution (H_2O_2 / H_2S = 1.5 – 2.5 molar ratio) was added. After the mixture (pH 11–12) had been allowed to react for 30 min, the thiocyanate content was measured by IC.

The amount of thiocyanate transformed from cyanide was obtained by the difference between sulfide-treated and non-treated samples. Thus, both thiocyanate and cyanide contents were determined.

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RESULTS AND DISCUSSION

Calibration and cyanide recovery

Calibration and recovery curves for cyanide and thiocyanate solutions are shown in Figure 1. The curves were obtained by measuring with IC (injection volume is 20 μL) for the standard thiocyanate solutions, standard cyanide solutions converted into thiocyanate and standard thiocyanate solutions treated by procedure I. These curves are not only linear but also coincide. This fact implies that the cyanide was converted to thiocyanate stoichiometrically, and the original SCN^- in the sample was not affected by reactions involved in Procedure I. Thus the recovery curves for cyanide and thiocyanate were coincident with the standard Calibration curve of thiocyanate.

Note that, if the injection volume was 100 μL, the detection limit of cyanide could be lower to 2.8×10^{-7} M (9 μg/L) and it was still 30 times more sensitive than the spectrophotometric method by using Fe^{3+} thiocyanate complex ($Fe(SCN)_3$).

Effect of pH on cyanide conversion efficiency

It was found that the formation of thiocyanate from the oxidation of cyanide with hydrogen peroxide in the presence of sulfide was significantly affected by pH. To investigate the pH effect, each solution (100 mL) containing cyanide (1.76×10^{-5}

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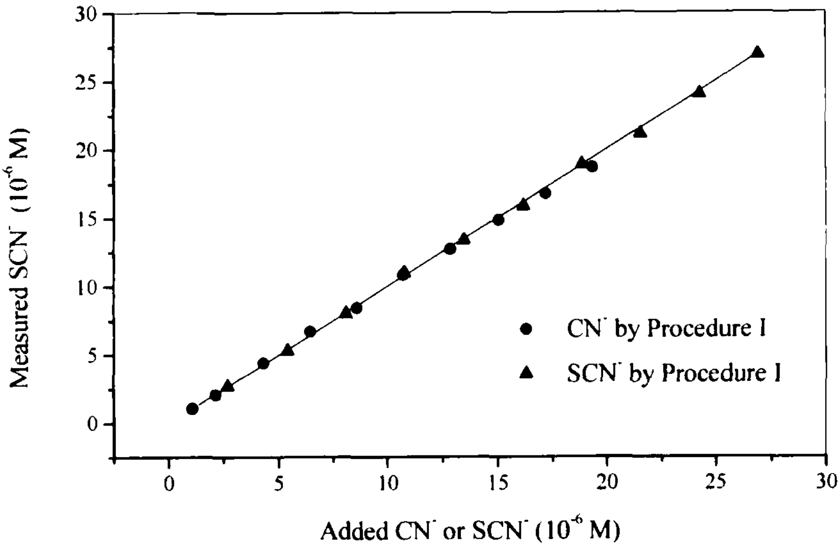

FIGURE 1 Calibration and recovery graphs for cyanide and thiocyanate

M), sulfide (3.44×10^{-2} M) and hydrogen peroxide (6.88×10^{-2} M) in buffers of various pH from 8.2 to 13.4 was allowed to react for 30 min. The thiocyanate formed from cyanide was quantified by IC with the conductivity detector.

As shown in Figure 2., the recovery of cyanide which is defined as [SCN^- detected / CN^- added] is 100 ± 2% when pH is in the range from 9.8 to 12.8. The recovery decreases rapidly when pH is lower than 9.8. This might be caused by the formation of molecular HCN and elementary S as depicted by reaction (2).

$$H_2O_2 + H_2S \rightarrow S + 2\ H_2O \qquad (2)$$

Regarding the decrease in recovery above pH 13.0, it is probably due to the increased oxidation strength of H_2O_2 at high pH values. Under these conditions, reactions (3) and (4) become significant. Thus, the cyanide cannot be converted completely to thiocyanate.

$$H_2O_2 + HCN \rightarrow HCNO + H_2O \qquad (3)$$

$$H_2S + 4\ H_2O_2 \rightarrow H_2SO_4 + 4\ H_2O \qquad (4)$$

It is clear that the pH of the reaction solutions should be adjusted to pH 11–12 under the conditions described in both Procedures I and II.

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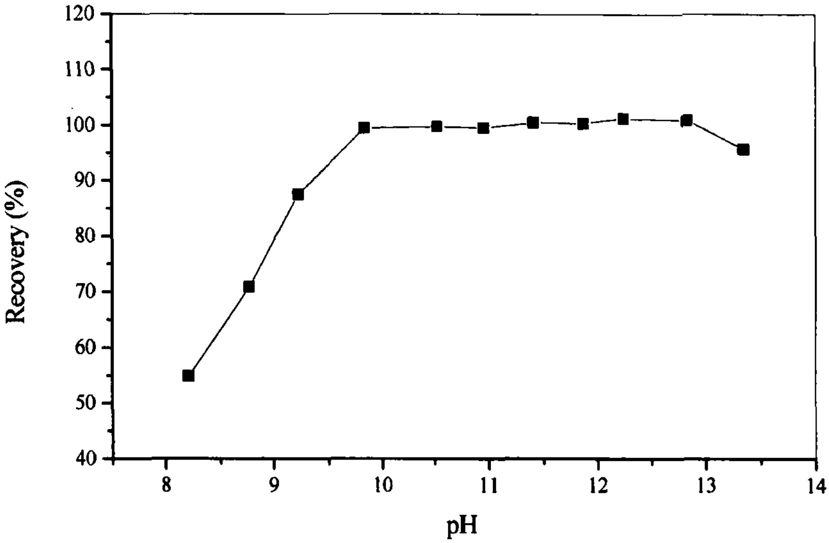

FIGURE 2 Effect of pH on the conversion efficiency of cyanide into thiocyanate. $CN^-=1.76\times10^{-5}$ M

Effect of sulfide and hydrogen peroxide dosages on the conversion efficiency of cyanide

The optimum dosages of sulfide and hydrogen peroxide required for the formation of thiocyanate were examined as follows. Each 10 mL of 1.72×10^{-5} M cyanide solution containing various amounts of sulfide and hydrogen peroxide was allowed to react for 40 min at pH 12. Figure 3 shows that the cyanide recovery is 100±2% when the molar ratio of H_2O_2 to H_2S is between 1.0 and 2.5 at sulfide concentrations of 2.91×10^{-2} to 8.75×10^{-2} M. The recovery decreases while the molar ratio of H_2O_2 to H_2S is larger than 2.5. It was probably caused by the formation of cyanate. On the other hand, when the molar ratio is lower than 1.0 the cyanide could not be converted completely to thiocyanate. Therefore, the molar ratio of H_2O_2 to H_2S should be maintained between 1.0 – 2.5 in the reaction solution under the conditions described in both Procedures I and II.

From Figure 3, it clearly indicates that procedure I should be followed when $[H_2S] < 0.03$ M.

Effect of reaction time on conversion efficiency

To determine the minimum reaction time required for the formation of thiocyanate, 40 mL of 2.12×10^{-5} M cyanide solutions containing 3.13×10^{-2} M sulfide

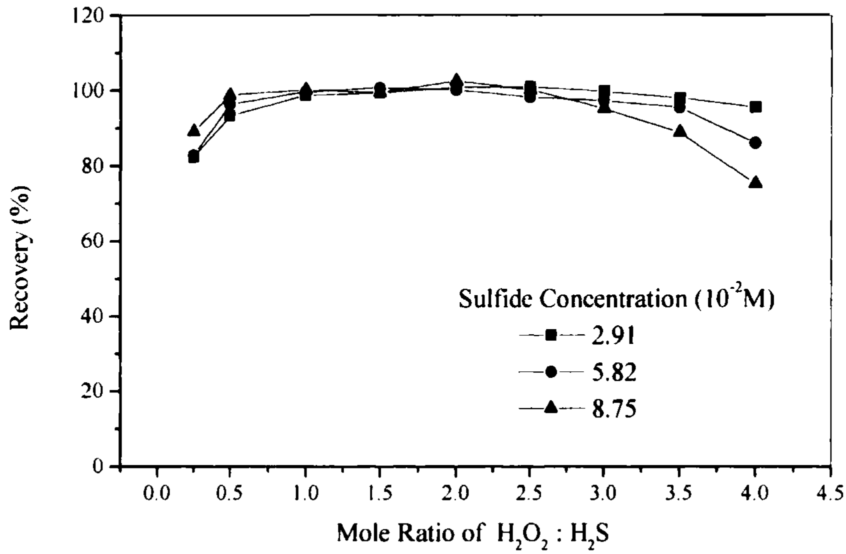

FIGURE 3 Effect of the dosages of sulfide and hydrogen peroxide on the conversion of cyanide into thiocyanate. $CN^- = 1.72\times10^{-5}$ M

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and various amounts of hydrogen peroxide were allowed to react at pH 12. Samples were taken and analyzed intermittently during the reaction period. Figure 4. shows that the reaction time required for the complete recovery of cyanide is less than 30 min when the molar ratio of H_2O_2 to H_2S was larger than 2.0.

Effect of foreign ions

Various kinds and amounts of foreign ions were separately added to glass vials, each of which contains 10 mL cyanide solution (4.19 μg of cyanide, 1.61×10^{-5} M) and the resulting solutions were analyzed by Procedure I. Table I. shows that the cyanide recovery is 100±2.5% in the presence of the tested foreign ions. Note that those foreign ions did not take part in the conversion of cyanide, and their peaks in the IC did not overlap with the peak of the thiocyanate. Hence, the existence of foreign ions did not interfere the measurement of cyanide.

Application to the field samples

Potential matrix interference from unknown species in the field samples from various refineries and research center was investigated by adding known amounts of cyanide to the samples and analyzing the resulting solutions as described in Procedures I and II. The results show that an average recovery of 98.7% was obtained with a standard deviation of ±2.0% for ten measurements with the additions of CN^-. It proves that the interference caused from the unknown species in the field samples can be ignored. Thus, this method can be a powerful tool to measure the cyanide content in the field samples accurately.

TABLE I Effect of foreign ions on the determination of 4.19 μg cyanide in a 10 mL solution

Ion	*Amount / μg*	*CN^- found / μg*	*Error %*
None	--	4.19	--
Br^-	10000	4.24	+1.2
Br^-	1000	4.16	–0.8
Cl^-	1000	4.14	-1.1
HCO_3^-	1000	4.25	+1.5
I^-	10000	4.16	–0.6
I^-	1000	4.22	+0.7
NH_4^+	1000	4.21	+0.4
NO_3^-	10000	4.20	+0.3
NO_3^-	1000	4.15	–0.9
PO_4^{3-}	10000	4.26	+1.7
$S_2O_3^{2-}$	10000	4.29	+2.4
$S_2O_3^{2-}$	1000	4.19	–0.1
SO_3^{2-}	10000	4.19	+0.02
SO_3^{2-}	1000	4.15	-1.0
SO_4^{2-}	10000	4.20	+0.2
SO_4^{2-}	1000	4.14	-1.2
$Fe(CN)_6^{3-}$	2000	4.25	+1.5

CONCLUSIONS

An analytical method has been developed to analyze free cyanide in FCC sour water containing high concentration of H_2S. In this method, the pretreatment to

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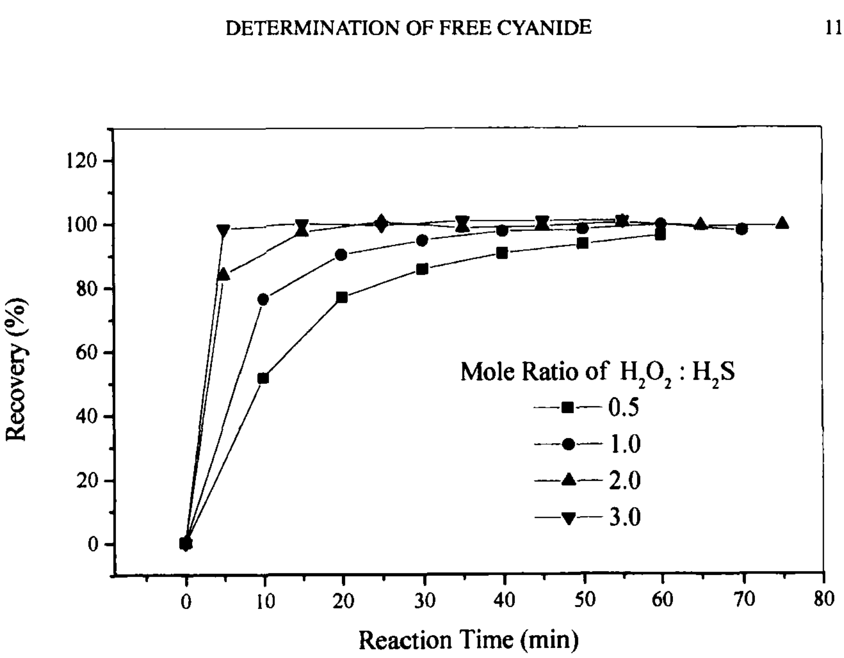

FIGURE 4 Effect of reaction time on the conversion efficiency of cyanide Into thiocyanate. $CN^- = 2.12\times10^{-5}$ M, $H_2S = 3.13\times10^{-2}$ M

remove the interference from H_2S is not required. Thiocyanate and free cyanide can be measured precisely and accurately. The detection limit for the free cyanide is 9 μg/L (2.8×10^{-7} M) and the standard error is ±2%. For low sulfide or non-sulfide containing samples, this method can also be applied by adding Na_2S artificially using Procedure I.

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