

Spectrophotometric Determination of Ni in Real Samples from Polyethylene Lined Tubing for Petroleum and Natural Gas Industries

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Abstract. Polyethylene lined tubing will be widely used in the exploitation of acid gas and oil wells. It was well known that nickel was an important element in polyethylene lined tubing. In this paper, a novel spectrophotometric method was described for determination of nickel in the polyethylene lined tubing. The method was based on the color reaction between nickel and dimethylglyoxime, which was favored in an alkaline medium, producing a red compound in the presence of ammonium persulfate as an oxidant. Under the optimum reaction conditions the absorption value was proportional to the concentration of nickel in the range of 0.080~0.60% ($R^2 = 0.9999$), and the relative standard deviation was less than 3.0% ($n=5$). The proposed method was applied successfully to determine nickel in polyethylene lined tubing samples.

1. Introduction

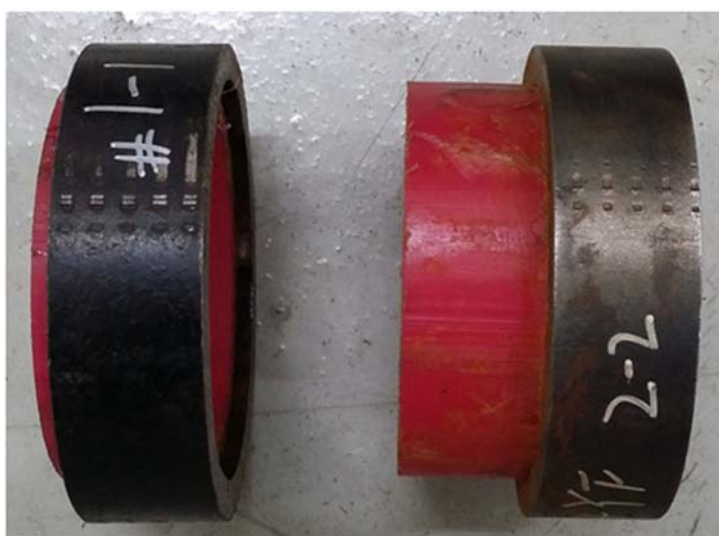


Figure 1. Polyethylene lined tubing samples



The condition of gas and oil wells in the west of China has complex characteristics such as deep, high temperature, high pressure, and serious corrosive that only corrosion-resistant tubing can be applied to explore. One key feature there is obvious existence of corrosive hydrogen sulfide medium. For example, the natural gas resource has reached as high as $4.19 \times 10^{12} \text{ m}^3$ in Sichuan area but nearly 70 percent fields contain high hydrogen sulfide medium and the highest content reaches 92 percent in weight. The sulfide stress corrosion failure frequently occurs due to absence of applicable technical specification which has led to huge economic damage. Statistical data showed that the average loss is 100 thousand dollar for the tubing failure. In some areas no suitable tubing can be supplied due to high hydrogen sulfide content. So there is obvious safety risk when tubing in these gas fields. Specification for tubing used in these regions was very necessary and urgent. The polyethylene lined tubing (Figure 1) has excellent resistance to corrosion. These composite pipes are key to enabling the industry to meet some of the energy security challenges that nations face today. Thus, polyethylene lined tubing will be widely used in the exploitation of acid gas and oil wells. The content of chemical elements in polyethylene lined tubing directly influences the properties of materials. In order to control the quality of polyethylene lined tubing products, the contents of trace impurities and alloy elements in polyethylene lined tubing should be determined. In making processes, the content of alloyed elements such as nickel, manganese, chromium, molybdenum, vanadium, and so on, is required to be strictly controlled because it fundamentally determines the performance of polyethylene lined tubing. It is well known that nickel is an important element in polyethylene lined tubing. Numerous analytical methods were employed for the determination of nickel in different types of matrices including atomic absorption spectrometry [1-3], atomic emission spectrophotometry [4, 5], molecular fluorescence spectroscopy [6], electroanalytical method [7] and spectrophotometry [8-14]. Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. Similarly, spectrophotometric methods also play an important role in nickel determination. The literatures shows that aromatic amines, azo dyes, oximes, porphyrins and other reagents have been used for the colorimetric determination of nickel. The most significant reagents are dimethylglyoxime, PAN-S and PAR, which is far more sensitive than the other two reagents. This present method was based on the color reaction between nickel and dimethylglyoxime, which was favored in an alkaline medium, producing a red compound in the presence of ammonium persulfate as an oxidant. The characteristic wavelength of maximum absorption was measured at 530 nm. Under the optimum reaction conditions the absorption value (A) was proportional to the concentration of nickel in the range of 0.080% ~ 0.60% ($R^2 = 0.9999$, mass fraction), and the relative standard deviation (RSD) was less than 3.0% ($n=5$). The proposed method was free from the interference from a large number of analytical important elements and has been applied satisfactorily to the determination of nickel in polyethylene lined tubing samples with the improved accuracy and precision, respectively. Results were in agreement with those attained by inductively coupled plasma atomic emission spectrophotometry at the 95% confidence level. The satisfactory performance in the determination of nickel in polyethylene lined tubing demonstrated that the method was practical and suitable not only for quality control analysis but also for product analysis, confirming the promise for polyethylene lined tubing research.

2. Experimental

2.1. Apparatus and reagents

A UV-visible spectrophotometer (Model TU-1901, Beijing Persee General Instrument Co. Ltd.) with 2.0-cm quartz cells was employed for all absorbance measurements. All chemicals including perchloric acid (Tianjin Tianda Reagent Plant), nitric acid (Xi'an Chemical Reagent Plant), ethanol (Tianjin Dongfang Reagent Plant) and hydrochloric acid (Sichuan Xilong Chemical Co. Ltd.) used in the experiments were of analytical reagent grade and were used as received. Solutions of ammonium persulfate (Tianjin Tianda Reagent Plant), sodium tartrate (Xi'an Chemical Reagent Plant) and sodium hydroxide (Institute of Shanghai Fine Chemical Materials) were prepared daily by dissolving the reagents in deionised water that treated with a Milli-Q water purification system (Millipore, Bedford,

MA, USA). Solution of dimethylglyoxime (Xi'an Chemical Reagent Plant) were prepared dissolving the reagents in ethanol, and the solutions of nickel were prepared from the steel certified reference materials (CRM) including GBW 01301, GBW 01302, GBW 01304, GBW 01306, GBW 454 (Institute of Anshan Iron and Steel Group Corporation), GBW 01354 (Institute of Fushun Iron and Steel Group Corporation). All working strength solutions in the experiment were prepared with deionised water.

2.2. General procedures

Weigh accurately 0.2000 g of drilled low alloy steel samples and dissolve the samples in 10 mL mixture acid solution of hydrochloric acid 25% (V/V) and nitric acid 25% (V/V) in a 150-mL taper bottle. Continue the treatment with mixture acid till the sample goes into solution. Add 5.0 mL perchloric acid (ρ 1.67 g·mL⁻¹) and heat to fumes of perchloric acid, and evaporate almost to dryness. Cool the solution, add 50 mL deionised water to dissolve some salts, and cool the solution at room temperature. Finally, dilute the solution in a 100-mL volumetric flask, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution 10.0 mL in a 50-mL volumetric flask, add 10 mL of 300.0 mg·mL⁻¹ solution of natrium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 10.0 mg·mL⁻¹ solution of dimethylglyoxime, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution in 2.0-cm quartz cells, this solution was the work solution. At the same time, transfer the first stock solution 10.0 mL in a 50-mL volumetric flask, add 10 mL of 300.0 mg·mL⁻¹ solution of natrium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 95% (V/V) ethanol, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution in 2.0-cm quartz cells, this solution was employed as the blank solution in subsequent experiments. Measure the absorbance at 530 nm using a UV-visible spectrophotometer with 2.0-cm quartz cells against a reagent blank prepared similarly. Plot the amount of nickel in the sample solution against absorbance to obtain the calibration graph.

3. Results and Discussion

3.1. Spectral characteristics

The absorption spectra of the reagents blank, nickel against the reagent blank were tested from 400 nm to 700 nm. The nickel yields the characteristic wavelength of maximum absorption at 530 nm wavelength. However, the absorption spectrum of the reagents blank under similar conditions shown that it does not absorb at 530 nm. And the experimentation also demonstrated that nickel increases the absorbance value considerably, resulting in increased sensitivity of the method. Therefore, measure the absorbance of nickel at 530 nm.

3.2. Select dissolved acid for low alloy steel samples

The effect of the different acids for dissolve the low alloy steel samples was examined. It was found that a solution mixed with 25% (V/V) hydrochloric acid and 25% (V/V) nitric acid has a good effect for dissolve the low alloy steel samples. Thus, an acid solution mixed with 25% (V/V) hydrochloric acid and 25% (V/V) nitric acid was recommended for dissolve the low alloy steel samples in subsequent studies.

3.3. Influence of the amounts of chromogenic reagent

Dimethylglyoxime was selected as the chromogenic reagent in the proposed method. The effect of the chromogenic reagent was examined by measuring the absorbance of solution containing certain amounts of nickel and variable amounts of dimethylglyoxime. It was found that 2.0 ml of 10.0 mg·mL⁻¹ dimethylglyoxime solution sufficed to complex the amounts of nickel taken; with higher concentrations the absorbance was essentially constant. Two milliliters of 10.0 mg·mL⁻¹ dimethylglyoxime solution were recommended as a suitable amount of chromogenic reagent.

3.4. Influence of the amounts of oxidant

Ammonium persulfate was selected as the oxidant in the proposed method. The effect of the oxidant was examined by measuring the absorbance of solution containing certain amounts of nickel and variable amounts of ammonium persulfate. It was found that 5.0 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate sufficed to oxidate the amounts of nickel taken, with higher concentrations the absorbance was essentially constant. Five milliliters of 40.0 mg·mL⁻¹ ammonium persulfate solution were recommended as a suitable amount of oxidant.

3.5. Sequence of addition of reagents

From experiments in which solution of sodium tartrate, solution of sodium hydroxide, solution of dimethylglyoxime and solution of ammonium persulfate were added in all possible orders. It was found that there was appreciable change in the colour of the solution and the variations in the absorbance values. The order of addition must be solution of sodium tartrate, solution of sodium hydroxide, solution of dimethylglyoxime and solution of ammonium persulfate.

3.6. Stoichiometry and stability constant

The stoichiometry of the nickel complex with dimethylglyoxime in solution was studied spectrophotometrically by Job's method of continuous variation and equilibrium shift method. The results indicate that the molar ratio of nickel to dimethylglyoxime is 1: 4. The molar extinction coefficient (ϵ) of the ligand complex is $1.3 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, which calculated from these results following the described method.

3.7. Interference studies

the extent of interference by diverse ions was determined by measuring the absorbance of solutions containing nickel and various amounts of diverse ions. The criterion for interference was an absorbance value varying by more than +2% from the expected value of nickel alone. The results show that a large excess of cations and anions which are usually associated in the determination of nickel do not interfere. The colorless metal ions do not interfere. The tolerable amounts of foreign species with respect to nickel for interference at +2% level were over 200~300 for the colored metal ions. When the colored metal ions contents of not more than 200~300 times nickel, it can be in some color solution adding a few drops of EDTA solution or sodium nitrite solution to fade the color, this solution as the measured reference solution to eliminate the interference. There was not obvious interference ions exist in polyethylene lined tubing.

3.8. Preparation of the calibration graph

Under the optimal conditions, a series of standard solutions of nickel were prepared by the different steel certified reference materials in a 100-mL volumetric flask. add 10 mL of 300.0 mg·mL⁻¹ solution of sodium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 10.0 mg·mL⁻¹ solution of dimethylglyoxime, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution in 2.0-cm quartz cells, this solution was the work solution. At the same time, transfer the first stock solution 10.0 mL in a 50-mL volumetric flask, add 10 mL of 300.0 mg·mL⁻¹ solution of sodium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 95% (V/V) ethanol, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Measure the absorbance at 530 nm using a UV-visible spectrophotometer with 2.0-cm quartz cells against a reagent blank. The absorbance of the solution was proportional to the concentration of nickel in the range of 0.080%~0.60% (mass fraction). Plot the amount of nickel in the sample solution against absorbance to obtain the calibration graph. The linear regression equation for nickel was $A = 1.20752C + 0.00198$, $R^2 = 0.9999$, and the relative standard deviation (RSD) was less than 3.0% (n=5).

4. Applications

4.1. Determination of nickel in polyethylene lined tubing samples

The recommended procedure has been applied satisfactorily to the determination of nickel in polyethylene lined tubing samples. The samples were dissolved according to the following procedure. Weigh accurately 0.2000 g of drilled low alloy steel samples and dissolve the samples in 10 mL mixture acid solution of hydrochloric acid 25% (V/V) and nitric acid 25% (V/V) in a 150-mL taper bottle. Continue the treatment with mixture acid till the sample goes into solution. Add 5.0 mL perchloric acid (ρ 1.67 g·mL⁻¹) and heat to fumes of perchloric acid, and evaporate almost to dryness. Cool the solution, add 50 mL deionised water to dissolve some salts, and cool the solution at room temperature. Finally, dilute the solution in a 100-mL volumetric flask, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution 10.0 mL in a 50-mL volumetric flask, add 10 mL of 300.0 mg·mL⁻¹ solution of sodium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 10.0 mg·mL⁻¹ solution of dimethylglyoxime, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution in 2.0-cm quartz cells, this solution was the work solution. At the same time, transfer the first stock solution 10.0 mL in a 50-mL volumetric flask, add 10 mL of 300.0 mg·mL⁻¹ solution of sodium tartrate, 10.0 mL of 100.0 mg·mL⁻¹ solution of sodium hydroxide, 2.0 mL of 95% (V/V) ethanol, 5 mL of 40.0 mg·mL⁻¹ solution of ammonium persulfate, followed make up to the mark with deionised water, mix well and let stand. Then, transfer the above stock solution in 2.0-cm quartz cells, this solution was employed as the blank solution in subsequent experiments. Measure the absorbance at 530 nm using a UV-visible spectrophotometer with 2.0-cm quartz cells against a reagent blank. The results were summarized in Table 1 with the good accuracy and precision.

Table 1. Results of determination of nickel in polyethylene lined tubing (ω , n=5)

Sample No.	A	RSD (%)	Content (%)	
			Proposed method	AES
1	0.1831	2.01	0.15	0.16
2	0.1590	1.87	0.13	0.15
3	0.1590	1.56	0.13	0.12
4	0.1469	1.35	0.12	0.12
5	0.1710	0.95	0.14	0.15
6	0.1590	2.33	0.13	0.13
7	0.1831	2.19	0.15	0.13
8	0.1710	2.38	0.14	0.13
9	0.1710	1.59	0.14	0.14
10	0.1469	1.24	0.12	0.13
11	0.2676	1.57	0.22	0.20
12	0.2797	0.85	0.23	0.22
13	0.2556	0.79	0.21	0.21
14	0.2556	1.94	0.21	0.23
15	0.2435	1.70	0.20	0.22
16	0.2797	2.34	0.23	0.24
17	0.2556	0.49	0.21	0.20
18	0.2797	1.02	0.23	0.22
19	0.2676	0.83	0.22	0.22
20	0.2797	1.36	0.23	0.24

5. Conclusion

Based on the chromogenic reaction between nickel and dimethylglyoxime, a simple and accurate spectrophotometric method for determination of nickel in polyethylene lined tubing was proposed. The red colored nickel solution exhibits absorption maximum at 530 nm. The proposed method was free

from the interference from a large number of analytical important elements and has been applied satisfactorily to the determination of nickel in polyethylene lined tubing samples. Compared with other methods for the determination of nickel, this method offers advantages of simplicity, less expensive instrumentation and high efficient. The satisfactory performance in the determination of nickel in polyethylene lined tubing demonstrated that the method was practical and suitable not only for quality control analysis but also for product analysis, confirming the promise for polyethylene lined tubing research.

Acknowledgments

The authors gratefully acknowledge the *State Key Laboratory for Performance and Structure Safety of Petroleum Tubular Goods and Equipment Materials*, and *CNPC Tubular Goods Research Institute*, and *China National Quality Supervision, Testing and Inspection Center of Oil Tubular Goods*.

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