An analytical method for the determination of molybdenum in the end fitting of PE flexible composite pipe

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Abstract. The flexible composite pipe is a new type of polymer composite pipe with excellent corrosion resistance. Based on the color reaction of molybdenum with sodium thiocyanate, a photometric method for the determination of molybdenum in flexible composite pipe joint samples was established. The sample is dissolved by a sulfuric acid-phosphoric acid mixed acid, and stannous chloride is used as a reducing agent in a sulfuric acid-perchloric acid medium, and an orange-red complex is formed between molybdenum and sodium thiocyanate, and the absorbance, absorbance and molybdenum content are measured in mass. The linear relationship is in the range of 0.30%~1.18%. This method uses a standard steel solution closer to the real sample to establish a working curve. The experiment shows that the method is accurate and simple. The molybdenum in the end fitting of flexible composite pipe was measured, and the results were satisfactory.

1. Introduction

As unconventional oil and gas resources continue to be developed, the problems and conditions facing oil and gas field development are becoming increasingly severe and demanding. Because unconventional oil and gas fields contain different concentrations of H2S, CO2 corrosive gases, SO42−, Cl−, Ca2+, Mg2+ ions and sulfate-reducing bacteria, iron bacteria, saprophytic bacteria, etc., under the combined action of these corrosive media, steel Conveying pipelines may be subject to severe corrosion damage, affecting the normal production of oil and gas fields. In order to meet the gathering and transportation requirements of such oil and gas wells, the gathering pipeline must use materials with excellent corrosion resistance. Because of this, various new composite pipes have been developed. The flexible composite pipe is a new type of polymer composite pipe with excellent corrosion resistance [1]. The flexible composite pipe has a multi-layer structure and is mainly composed of a thermoplastic inner liner layer, a reinforcing layer and an outer protective layer. The inner liner is polyethylene, crosslinked polyethylene, polyvinylidene fluoride or other thermoplastics. The inner liner acts as a seal and resistant to chemical attack. The reinforcing layer is a material such as polyester fiber, glass fiber, aramid fiber, carbon fiber, steel wire, steel strip or the like which is woven or wound on the inner liner. The reinforcing layer acts as a pressure bearing. The outer protective layer is made of polyethylene resin. The outer protective layer acts to prevent wear and external corrosion. The advantages of flexible composite pipes are shown in the following aspects. The flexible composite pipe has high corrosion resistance. The inner
The wall of the flexible composite pipe is not easy to be fouled, and the coefficient of frictional resistance is relatively low, and the application effect in the high salinity oil and gas field is very satisfactory. The flexible composite pipe has better flexibility and can effectively reduce the influence of pipe bending caused by terrain fluctuations and address faults. The flexible composite pipe is convenient to store and can be used as an emergency pipeline. The emergency cost and emergency response capability are strong. The length of the flexible composite pipe can be produced according to actual needs, and the general length is 100 m~300 m. The flexible composite pipe is connected by a metal fitting at its end (Figure 1). Metal fitting is an important part of flexible composite pipes. The content of each chemical element in the metal fitting directly affects the properties of the material. Therefore, accurate detection of the chemical composition of flexible composite pipe fitting and quality control are important guarantees for the development, application and production of flexible composite pipes.

Figure 1. End-fitting of flexible composite pipe

The addition of molybdenum as an alloying element can increase the strength of the steel without reducing the plasticity and toughness of the steel. At the same time, molybdenum can make the steel have sufficient strength at high temperature and improve the corrosion resistance and cold brittleness of the steel. Molybdenum exists mainly in the form of carbide (Mo2C) in steel, and the content of molybdenum in structural steel is about 1%; in heat-resistant steel and tool steel, 0.15%~0.7% of molybdenum is often added; while in some heat-resistant and acid-resistant In anti-alkaline corrosion and other stainless steels and some high-speed steels and high-temperature alloys, the content of molybdenum can be as high as 5% to 9%. As an important chemical component in the end fitting of flexible composite pipe, molybdenum is important for the control of its content. The main methods for detecting molybdenum in steel materials include spectrophotometry [2, 3], atomic absorption spectrometry [4, 5], fluorescence spectroscopy [6], polarographic methods [7, 8] and high performance liquid chromatography [9]. Spectrophotometric determination of molybdenum is generally based on the formation of colored complexes of molybdenum ions and chromogenic agents. The reported chromogenic reagents include thiocyanate [10], catechol violet [11], and decenyl fluorescence. Ketone [12] and 3, 5-dibromo-4-aminophenylfluorone [13]. In recent years, some scholars have used traditional spectrophotometry and chemometric methods to determine the content of molybdenum in steel. These combined chemometric methods include artificial neural network [14] and partial least squares [15]. In this paper, based on the color reaction of molybdenum with the developer sodium thiocyanate, a photometric method for the determination of molybdenum in the end fitting of flexible composite pipe
was established. The sample is dissolved by a sulfuric acid-phosphoric acid mixed acid, and iron and molybdenum are reduced by stannous chloride in a sulfuric acid-perchloric acid medium, and an orange-red complex is formed by molybdenum and sodium thiocyanate, and is measured at a wavelength of 470 nm by a spectrophotometer. The absorbance, absorbance and molybdenum content are linear in the range of 0.30%~1.18%. This method uses the standard steel solution with different molybdenum content to establish the working curve, which is closer to the real sample. The experiment shows that the method is accurate, simple, low cost, practical and popular, and has been measured in the end fitting of flexible composite pipe. The measurement results are satisfactory.

2. Experimental

2.1. Apparatus and reagents
TU-1901 UV-visible spectrophotometer (Beijing General Instrument Co., Ltd.). Sulfuric acid (1.84 g mL\(^{-1}\), Xi'an Chemical Reagent Factory); Phosphoric acid (1.69 g mL\(^{-1}\), Sichuan Chemical Co., Ltd.); Sulfuric acid-phosphoric acid mixed acid: 150 mL of sulfuric acid is slowly added to 700 mL in water, after a little cold, add 150 mL of phosphoric acid and mix; nitric acid (1.42 g mL\(^{-1}\), Xi'an Chemical Reagent Factory); hydrochloric acid (1.19 g mL\(^{-1}\), Xi'an Chemical Reagent Factory); perchloric acid (1.67 g mL\(^{-1}\), Tianjin Chemical Plant); Sodium thiocyanate (Xi'an Chemical Reagent Factory): Dissolve 10.0 g of sodium thiocyanate in a 250 mL beaker, and then prepare a 100.0 mg mL\(^{-1}\) solution in a 100 mL volumetric flask; Stannous chloride (Xi'an Chemical Reagent Factory): Weigh 10.0 g of stannous chloride in a 250 mL beaker, add 10 mL of hydrochloric acid, heat to dissolve and boil, and cool to make 100.0 mg mL\(^{-1}\) in a 100 mL volumetric flask. Molybdenum standard solution: GBW01308, GBW01310, GBW01311 (Anshan Iron and Steel Research Institute, standard material), YSBC11217, YSBC11238 (Steel Research Institute, Standard Substance), YSBC18202a, YSBC18206a (Heavy Steel Research Institute, standard Substance), B59 (Fushun Steel Research Institute, standard material). The reagents used in the experiment were all analytically pure, and the water used in the experiment was secondary deionized water.

2.2. Procedures
Weigh 0.2500 g sample into a 250 mL Erlenmeyer flask, add 40 mL of the above-mentioned sulfuric acid-phosphoric acid mixed acid, heat until the sample is completely dissolved, add nitric acid to destroy the carbide, continue heating and evaporate to sulfuric acid smoke for 2 min~3 min. After cooling, add 20 mL of water and heat to dissolve the salts. After cooling, transfer to a 100 mL volumetric flask, dilute to the mark with water, and mix. Pipette 10.00 mL of the sample solution into a 50 mL volumetric flask, and then add 4 mL of 50% (V/V) sulfuric acid, 10 mL of 17% (V/V) perchloric acid, and mix. Add 10 mL of 100.0 mg mL\(^{-1}\) sodium thiocyanate solution, mix well, add 10 mL of 100.0 mg mL\(^{-1}\) stannous chloride solution and dilute with 5% (V/V) sulfuric acid while shaking. Mix to the mark and mix. This solution is a color developing solution. Another 10.00 mL sample solution was placed in a 50 mL volumetric flask, followed by 4 mL of 50% (V/V) sulfuric acid, 10 mL of 17% (V/V) perchloric acid, and mixed. Add 10 mL of 100.0 mg mL\(^{-1}\) stannous chloride solution while shaking, dilute to the mark with 5% (V/V) sulfuric acid, and mix. Use this solution as the reference solution. After standing for 10 min~15 min, the developed solution was placed in a 2 cm cuvette, and the absorbance was measured on a spectrophotometer at a wavelength of 470 nm using the reference solution as a reference.

3. Results and discussion

3.1. Absorption curve
According to the experimental method, the TC-1902 UV-visible spectrophotometer was used to scan the developed standard solution in the wavelength range of 400 nm to 700 nm. The results showed that the color reaction of molybdenum with thiocyanate ion produced an orange-red complex. The maximum
absorption peak of the compound is at a wavelength of 470 nm. Therefore, the method selects the absorbance measurement at a wavelength of 470 nm.

3.2. Dissolved acid
Both sulfuric acid and phosphoric acid can dissolve the sample. Molybdenum is insoluble in hydrochloric acid, and the sample is passivated by dissolving the sample with concentrated nitric acid. It has been found that 15% (V/V) sulfuric acid and 15% (V/V) are selected. The mixed acid dissolves the sample.

3.3. Chromogenic reagent
This method uses sodium thiocyanate as a color developer. The molybdenum standard solution was selected, and the absorbance was measured according to the experimental method with different amounts of sodium thiocyanate solution. It was found that the absorbance of the system reached the maximum when the dosage of 100.0 mg mL\(^{-1}\) sodium thiocyanate solution was 10 mL. Stable. Therefore, the amount of developer selected for the experiment was 2 mL of 100.0 mg mL\(^{-1}\) sodium thiocyanate solution.

3.4. Select reductant
When ascorbic acid is used as the reducing agent, the color reaction of molybdenum with thiocyanate ion is slow, and it takes 2 h at room temperature. When stannous chloride with strong reducing ability is used as reducing agent, molybdenum and sodium thiocyanate are used. The color reaction rate is greatly accelerated, and the reaction can be completed within 10 min to 15 min. In this method, stannous chloride is selected as the reducing agent, and the acidity of the reaction medium is controlled by 4 mL 50% (V/V) sulfuric acid and 10 mL 17% (V/V) perchloric acid. Among them, perchloric acid can act as a reduction inhibitor, and Mo(VI) is not excessively reduced to Mo(III) which does not participate in the color reaction.

3.5. Stoichiometry and stability constant
The experiment shows that under room temperature, molybdenum and sodium thiocyanate can form an orange-red complex in 10 min~15 min and completely develop color. After the color development is complete, the system can be stabilized for at least 1 h. The complex formed by the chromogenic reaction by the molar ratio method and the equimolar continuous conversion method is \([\text{MoO(SCN)}_5]^{2-}\), and the molar ratio of molybdenum to thiocyanate is 1:5, and the orange-red complex. The molar absorption coefficient of the substance, \(\varepsilon = 1.75 \times 10^4\) L mol\(^{-1}\) cm\(^{-1}\).

3.6. Interference
It was found by interference test that the metal ions which are generally colorless and the metal ions which do not undergo complexation reaction with the thiocyanate ions do not interfere with the measurement. When the amount of copper in the test solution is less than 0.2 mg, the amount of vanadium is less than 0.05 mg, the amount of cobalt is less than 0.8 mg, the amount of antimony is less than 0.8 mg, and the amount of chromium is less than 2.4 mg, there is no effect on the determination. The content of copper, vanadium, cobalt, antimony and chromium in the flexible composite pipe joint sample in this research work is far less than the above interference upper limit, and thus does not interfere with the determination.

3.7. Preparation of the calibration graph
Under the selected experimental conditions, weighed 0.2500 g of a series of different molybdenum contents, placed in a 250 mL Erlenmeyer flask, added 40 mL of sulfuric acid-phosphoric acid mixed acid, heated until the sample was completely dissolved, and added dropwise. Nitric acid destroys the carbide and continues to evaporate to sulfuric acid smoke for 2 min~3 min. Slightly cold, add 20 mL of water to heat the salt, cool it, transfer it to a 100 mL volumetric flask, dilute to the mark with water, and
mix well. Take 10.00 mL of the sample solution in a 50 mL volumetric flask. The following procedure is to prepare a series of standard steel solutions according to the experimental procedures, and measure the absorbance of the solution at a wavelength of 470 nm. When the molybdenum content is in the range of 0.30%~1.18%, the molybdenum content of the standard steel solution is linear with its corresponding absorbance. The mass fraction of molybdenum in the standard steel is the abscissa and the corresponding absorbance is the ordinate, and the working curve is established. The linear regression equation was: \( A = 0.66C + 0.011 \). \( R^2 = 0.9999 \), and the relative standard deviations were all less than 3.0%.

4. Applications
Accurately weigh 0.2500 g sample, place it in a 250 mL erlenmeyer flask, add 40 mL of sulfuric acid-phosphoric acid mixed acid, heat until the sample is completely dissolved, add nitric acid to destroy the carbide, continue heating and evaporate to sulfuric acid smoke for 2 min~ 3 min. Slightly cool, add 20 mL of water to heat the salt, cool it, transfer it to a 100 mL volumetric flask, dilute to the mark with water, and mix well. Take 10.00 mL of the sample solution in a 50 mL volumetric flask, strictly follow the experimental procedure, measure the absorbance at 470 nm on a spectrophotometer, and find the molybdenum content of the sample on the working curve in table 1, at the same time, the inductively coupled plasma atomic emission spectrometry (ICP-AES) in the national standard method was used for sample analysis, and the two methods achieved good consistency. It can be seen from the measurement results that the method has good accuracy and precision.

Table 1. Results of determination of molybdenum in end fitting \(^a\)

| Sample No. | Size (mm) | \( A \) | RSD (%) | Content (\( \omega, \% \)) |
|------------|-----------|--------|---------|--------------------------|
|            |           |        |         | By the proposed method    | By AES         |
| 1          | DN80      | 0.6744 | 0.52    | 1.00                     | 1.01           |
| 2          | DN80      | 0.6877 | 0.96    | 1.02                     | 0.99           |
| 3          | DN80      | 0.6678 | 1.24    | 0.99                     | 1.00           |
| 4          | DN80      | 0.6943 | 1.67    | 1.03                     | 1.03           |
| 5          | DN80      | 0.6942 | 0.67    | 1.03                     | 1.01           |
| 6          | DN80      | 0.6810 | 2.01    | 1.01                     | 1.04           |
| 7          | DN75      | 0.5084 | 1.30    | 0.75                     | 0.75           |
| 8          | DN75      | 0.5283 | 1.98    | 0.78                     | 0.76           |
| 9          | DN75      | 0.5350 | 2.00    | 0.79                     | 0.76           |
| 10         | DN75      | 0.5150 | 2.67    | 0.76                     | 0.79           |
| 11         | DN75      | 0.5084 | 0.64    | 0.75                     | 0.78           |
| 12         | DN75      | 0.5151 | 1.63    | 0.76                     | 0.76           |

Notes: \(^a\) The average of five determinations.

5. Conclusion
In this paper, the spectrophotometric method for the determination of molybdenum in the end fitting of flexible composite pipe was studied. The method uses a sulfuric acid-phosphoric acid mixed acid to dissolve the sample, and reduces the molybdenum with stannous chloride in a sulfuric acid-perchloric acid medium, and uses a standard steel solution with different molybdenum content based on the color reaction of sodium thiocyanate and molybdenum. A working curve is established with a linear range of 0.30% to 1.18%. The method was applied to determine the molybdenum in the flexible composite pipe joint, and the measurement results were satisfactory. Experiments show that the photometric method
has high accuracy and precision, good selectivity, simple operation process and low cost, and has practical and popular value. These features make the method useful for component analysis and quality control of flexible composite pipe.

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References
[1] K. Yu, E.V. Morozov, M.A. Ashraf, Analysis of flexural behaviour of reinforced thermoplastic pipes considering material nonlinearity, Compos. Struct. 119 (2015) 385-389.
[2] A. Kumar, R. Dass, A rapid spectrophotometric method for micro-determination of molybdenum in alloy steels and environmental samples, Chem. Anal. 53 (2008) 617-625.
[3] L. Zhang, W. Cao, Y. Fu, Spectrophotometric determination of molybdenum with nitrosalicylfluorone, PTCA: Chem. Anal. 43 (2007) 751-752.
[4] X. Xu, Determination of molybdenum in chloride steel by atomic absorption spectrometry, Metal Mine. 2005, 40 (5): 34-35.
[5] Z. Gao, Y. Li, Y. Wang, Determination of molybdenum in steel by calcium fluoride sensitized graphite furnace atomic absorption spectrometry, Metal. Anal., 16 (1996) 17-20.
[6] H. Ma, G. Qi, Study on the determination of molybdenum by fluorescence quenching method of fluorophenylfluorone-cetylpyridinium bromide, Metal. Anal. 21 (2001) 15-17.
[7] Z. Jiang, Z. Huang, Study and application of catalytic differential polarography for trace molybdenum, J. Guangxi Normal University Natural Sci. 14 (1996) 52-57.
[8] G. Yan, J. Luo, A. Tan, Determination of trace molybdenum in steel by oscillographic method of fluorophenylfluorone-cetylpyridinium bromide, Metall. Anal. 43 (2003) 445-447.
[9] B. Tang, X. Hu, H. Wang, Determination of tungsten and molybdenum in steel and alloy by high performance liquid chromatography, PTCA: Chem. Anal. 39 (2003) 445-447.
[10] M. Zhang, Determination of titanium and molybdenum in stainless steel, Special Steel Tech. 12 (2004) 16-19.
[11] S. Yu, Y. Lu, Simultaneous photometric determination of tungsten and molybdenum in steel samples by multi-wavelength linear regression, J. Rare Metal. 21 (1997) 149-152.
[12] Q. Xu, D. Wang, X. Li, Synthesis of a new reagent, decenyl fluorone and its spectrophotometric determination of molybdenum in alloy steel, J. Metal. 18 (1998) 45-46.
[13] Y. Huang, H. Zhang, Q. Li, dissociation of fluorone and its color reaction with molybdenum, Wuhan University J. 41 (1995) 672-676.
[14] H. Zhao, J. Li, H. Yu, Simultaneous determination of tungsten, molybdenum and titanium by genetic neural network-spectrophotometry, Metal. Anal. 27 (2007) 18-21.
[15] Q. Wu, Y. Ding, Simultaneous determination of molybdenum and titanium by high-sensitivity fourth-order derivative spectrum, Spectroscopy Spectral Anal. 15 (1995) 119-124.