Analysis of trace organics and its correlation with COD in condensate from natural gas to hydrogen production

Peipei Fan, Lin Zhang, Zongjian Liu, Weidong Zhang, Qun Cui and Haiyan Wang

ABSTRACT

Qualitative and quantitative analysis of trace organics in the condensate and its correlation with chemical oxygen demand (COD) is the key to the research on the reuse technology of condensate (condensate) from natural gas to hydrogen production process. The contents of anions, COD, total organic carbon (TOC) and total nitrogen (TN) were measured by ion chromatography and the TOC analyzer. Trace organics in the condensate and its correlation with COD was investigated in this paper. Results show that the contents of COD and TOC is 74.1 and 17.81 mg/L, respectively, and the anions in the condensate are mainly Cl\(^-\), I\(^-\), and SO\(_4^{2-}\), etc. The condensate mainly contains small molecule organics including methanol, ethanol and formic acid with the content of 41.4, 2.1 and 3.2 mg/L, respectively. The spiked recovery of methanol, ethanol and formic acid is 96.1%, 100.2% and 103.9% by high performance liquid chromatography (HPLC) and gas chromatography (GC), respectively. Methanol is the main source of COD in the condensate, and the contribution rate reaches up to 83.8%. The removal of trace methanol can significantly reduce the COD of the condensate. This work might provide basic data for reasonable recovery and utilization of condensate in the hydrogen production process.

Key words | COD, condensate from natural gas to hydrogen production, formic acid, gas chromatography, high performance liquid chromatography, methanol

HIGHLIGHTS

- Quantitative analysis of trace organics in the condensate is the key to their deep purification.
- Correlation between trace organics and COD was investigated.
- Trace organics in the condensate are methanol, ethanol and formic acid.
- The contribution rate of methanol for COD reaches up to 83.8%.
- The removal of organics can significantly reduce the COD of the condensate.

INTRODUCTION

Excess steam is added to improve the reaction conversion rate in the steam conversion process for natural gas to hydrogen production. The excess steam after the reaction is cooled and separated to generate condensate of the hydrogen production process (referred to as the condensate). The condensate was originally designed as a feed water for the waste heat boiler system to generate steam. Part of the condensate was then used in the hydrogen production reaction, and the rest went to the steam pipe network. However, there exist trace organics in the condensate (Choudhary et al. 2001; Lou et al. 2019); the accumulation of organics in the recycling process could easily affect the stability of the boiler and the steam quality of external pipe network. Currently, only a small amount of the condensate is reused as the feed water for the boiler, and the rest is discharged into the circulating water system. A lot of condensate from...
a large scale hydrogen unit was always discharged into the circulating water system, which led to a rise in chemical oxygen demand (COD) and the growth of bacteria (Zhang 2011) in the circulating water system. This might affect the safety and stable operation of the circulating water system. Consequently, a large amount of condensate had to be directly discharged into the sewage system, resulting in a waste of high-quality water resource and energy. Therefore, a reasonable recovery and utilization process of condensate was urgently needed to solve the problem for the related enterprises. Our group (Wang 2014) had developed an adsorption and purification technology of the condensate from hydrogen production process, and the condensate can meet the feed water requirements of the boiler after purification. Analysis of trace organics in the condensate is the key to deep purification. Luo et al. (2016) studied the determination method of trace organics in the condensate from syngas production. Formic acid and acetic acid were the main organics in the condensate, and 91% of the organic carbon (TOC) in the condensate is derived from formic acid.

With the development of the natural gas to hydrogen production process and catalyst technology, the conversion rate of methane (Hallajbashi & Shahraki 2013) has been significantly improved and the content of organics in the condensate has been reduced to trace, which results in the quantitative analysis of the trace organics being more difficult. Nowadays, COD is the only determination of the condensate in industrial production, and there are few reports on the analysis of trace organics (small molecule alcohols and acids). Guo (2006) found that the COD of the acidic condensate of the hydrogen production unit was no more than 20 mg·L⁻¹. Xu et al. (2006) found the COD of the condensate of light oil cracking of the hydrogen production was 10 mg·L⁻¹. Jiao et al. (2009) found that the COD of the condensate in the light naphtha steam conversion to hydrogen production unit in an aromatics plant was 200 mg·L⁻¹. Wang (2008) analyzed that the COD of the condensate from natural gas to syngas condensate was 102.1–106.5 mg·L⁻¹, and there existed methanol, formaldehyde, formic acid and methylal in the condensate. In short, the determination of trace organics in the condensate of hydrogen conversion process is limited to the theoretical and qualitative analysis, and relevant quantitative analysis research has not been reported.

The COD in the condensate of the natural gas to hydrogen production is less than 200 mg·L⁻¹. The determination of COD by potassium dichromate method is affected by the contents of reducing ions (such as Cl⁻ and NH₄⁺, etc.) and trace organics in the solution. Byung (1989) found that when Cl⁻ and NH₃ were both present in the aqueous solution, 1 mg·L⁻¹ NH₃ was equivalent to 4.57 mg·L⁻¹ COD, and using low concentration potassium dichromate (0.025N K₂Cr₄O₇) could better avoid the interference of NH₃ on the determination of COD. Chen & Jia (2013) found the COD in an aqueous solution that was measured by the potassium dichromate method; the COD was mainly derived from organics, Cl⁻, NH₃ (or NH₄⁺) and other reductive substances. The COD generated by 1 mg·L⁻¹ Cl⁻ is 0.23 mg·L⁻¹. Bi et al. (2017) studied the effects of inorganic ions (Cl⁻ and F⁻) and dissolved organics (humic acid (HA) and fulvic acid (FA)) on the COD in the water body of Cheng Hai. The content of COD and Cl⁻ (0–30 mg·L⁻¹) were significantly linearly related. When the contents of FA and HA and Cl⁻ range from 2 to 30 mg·L⁻¹ in the mixed solution, the presence of a certain concentration of Cl⁻ enhanced the influence of FA and HA on the determination of COD. The COD of the mixed solution was higher than that of the single solution of FA, HA and Cl⁻.

The relationship analysis between the COD and the compositions of trace organics in the condensate can provide research directions for purification treatment. Yin et al. (2015) found that the increase of the content of methanol in the circulating water of the methanol production unit would cause the increase of COD from 26 to 352 mg·L⁻¹. Li et al. (2017) found the content of methanol in the low-temperature methanol washing wastewater and rectification wastewater of coal chemical industry could quickly quantified the COD value. The content of methanol in the wastewater was 100–10,000 mg·L⁻¹, the linear equation ratio between the COD measured by the potassium dichromate method and the calculated COD by the concentration of methanol was 0.90–1.11. Wang (1996) studied the relationship between the contents of acetaldehyde, acetic acid and ethylene glycol and COD in aqueous solution. The COD was linearly related to the content of acetaldehyde (0–54 mg·L⁻¹), acetic acid (0–1,000 mg·L⁻¹) and ethylene glycol (0–1,000 mg·L⁻¹), and the ratio between the COD and the content of acetaldehyde, acetic acid and ethylene glycol was 1.87, 0.95 and 1.24, respectively.

From the above, there are no reports on the correlation analysis between small molecule organics (carboxylic acids and alcohols) and COD in the condensate of natural gas to hydrogen production process. Therefore, the content of total organic carbon (TOC), inorganic carbon (IC) and total nitrogen (TN) in the condensate was determined using a TOC analyzer. Qualitative and quantitative of the trace organics were analyzed by high performance liquid chromatography (HPLC) and gas chromatography (GC). The relationship
between the trace organics and COD in the condensate was explored. It will provide basic data for the development of purification treatment technology for condensate.

**EXPERIMENTAL**

**Raw materials and main reagents**

The condensate from natural gas to hydrogen production was provided by a petrochemical company. The main reagents are shown in Table 1.

**Composition analysis methods of condensate**

**Determination of COD content**

According to the standard of ‘Determination of Chemical Oxygen Demand in Water Quality Rapid Digestion Spectrophotometry’ (HJ/T399-2007), the COD of the condensate was analyzed by colorimetry using a COD analyzer (ET99730 from Lovibond, Germany).

**Determination of total carbon and nitrogen content**

The contents of TOC and TN in the condensate were analyzed using a TOC analyzer (Multi-C/N-3100 from Analytik Jena, Germany) equipped with a non-dispersive infrared detector. The reaction gas was oxygen (99.99%) with a flow rate of 160 mL·min⁻¹ and a pressure of 0.4 MPa. The temperature of the furnace was 800 °C and the sample injection volume was 500 μL.

**Determination of anions**

The types and contents of anions in the condensate were determined by ion chromatography (Metrohm883 of Metrohm) equipped with an A5-250 column (250 mm × 4 mm × 5 μm) and a conductivity detector. The test temperature was 25 °C, and the sample injection volume was 20 μL with a flow rate of 0.7 mL·min⁻¹.

**Analysis of trace methanol and ethanol**

The contents of methanol and ethanol were determined using an Agilent 7890A gas chromatograph equipped with a FFAP column (0.32 mm × 50 m × 0.33 μm) and a flame ionization detector (FID). The injection volume of the sample was 4.0 L. The initial column temperature was 50 °C, maintained for 4 min, and then heated to 100 °C at a rate of 15 °C·min⁻¹. The temperatures of the detector and the vaporization chamber were both 200 °C. The carrier gas was high purity nitrogen (99.999%) with a flow rate of 40 mL·min⁻¹, and the shunt ratio was 20:1.

**Analysis of trace formic acid**

The content of formic acid was determined using Shimadzu LC-20A high performance liquid chromatography equipped with an InertSustain C18 column (4.6 mm × 250 mm × 5 μm). The column temperature was 35 °C, the injection volume was 10 μL and the detection wavelength was 210 nm, respectively. The mobile phase was acetonitrile and potassium dihydrogen phosphate aqueous solution (a volume ratio of 5:95) with a flow rate of 1.0 mL·min⁻¹, in which the content of potassium dihydrogen phosphate was 0.03 mol·L⁻¹ (pH of 1.5).

**Determination of spiked recoveries**

The spiked samples of formic acid were obtained by adding 5 mL formic acid standard solutions (2.0, 4.0 and 8.0 mg·L⁻¹, respectively) into three 5 mL condensates. Similarly, the spiked samples of methanol and ethanol were gained by adding 5 mL of methanol standard solutions (16.0, 32.0 and 40.0 mg·L⁻¹, respectively) and ethanol standard solutions (1.0, 2.0 and 4.0 mg·L⁻¹, respectively) into three 5 mL condensates, respectively. The spiked recovery (P) were calculated by Equation (1).

\[
P = \frac{C_2 \times V_2 - C_1 \times V_1}{C_0 \times V_0} \times 100\%
\]
where $P$ (%) is the spiked recovery, $C_0$ (mg·L$^{-1}$) is the content of formic acid/methanol/ethanol in the standard solution, $C_1$ (mg·L$^{-1}$) is the content of formic acid/methanol/ethanol in the condensate, $V_0$ (mL), $V_1$ (mL) and $V_2$ (mL) are the volume of the standard solution, condensate and spiked sample, respectively.

## RESULTS AND DISCUSSION

### Composition analysis of condensate

The content of COD and TOC (the difference between TC and IC) in the condensate was analyzed using a COD and TOC analyzer. The contents of anions were determined by ion chromatography. The results are shown in Table 2.

It can be seen from Table 2 that the COD of the condensate was 74.1 mg·L$^{-1}$. The content of TOC was 17.81 mg·L$^{-1}$, accounting for about 80% of the content of TC (22.87 mg·L$^{-1}$). Anions in the condensate were $\text{Cl}^-$, $\text{I}^-$, $\text{SO}_4^{2-}$, $\text{CH}_3\text{COO}^-$ and $\text{HCOO}^-$. Among them, the content of $\text{Cl}^-$ and $\text{I}^-$ was 1.42 and 7.82 mg·L$^{-1}$, respectively. The content of $\text{HCOO}^-$ and $\text{CH}_3\text{COO}^-$ was 3.13 and 0.17 mg·L$^{-1}$, respectively.

### Analysis of organic acids in the condensate

The analysis via ion chromatography shows that there were existed trace formic acid and acetic acid in the condensate. Therefore, based on the optimized testing conditions of HPLC, the trace organic acids in the condensate were qualitatively and quantitatively analyzed.

#### Qualitative analysis

The HPLC chromatogram of ultrapure water, condensate, mixed standard solutions of formic acid (2.5 mg·L$^{-1}$) and acetic acid (1.5 mg·L$^{-1}$) is shown in Figure 1.

As shown in Figure 1, the retention time of formic acid and acetic acid is 3.4 and 4.4 min, respectively. There was no characteristic peaks of formic acid and acetic acid in ultrapure water. The main small-molecule organic acid in the condensate is formic acid with no obvious acetic acid peak, indicating the content of acetic acid is almost close to the detection limit of HPLC.

#### Quantitative analysis of formic acid

**Standard curve of formic acid.** Refer to China GB/T602-2002, standard solutions of formic acid with the contents of 0.8, 1.0, 2.0, 4.0 and 8.0 mg·L$^{-1}$ were prepared, and the standard curve of formic acid was determined. The results are shown in Figure 2.

As shown in Figure 2, when the content of formic acid is in the range of 0.8–8 mg·L$^{-1}$, the peak area (y) and the

<table>
<thead>
<tr>
<th>Water quality index</th>
<th>Content, mg·L$^{-1}$</th>
<th>Anions</th>
<th>Content, mg·L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>74.1</td>
<td>$\text{CH}_3\text{COO}^-$</td>
<td>0.17</td>
</tr>
<tr>
<td>TC</td>
<td>22.87</td>
<td>$\text{HCOO}^-$</td>
<td>3.13</td>
</tr>
<tr>
<td>IC</td>
<td>5.06</td>
<td>$\text{Cl}^-$</td>
<td>1.42</td>
</tr>
<tr>
<td>TOC</td>
<td>17.81</td>
<td>$\text{I}^-$</td>
<td>7.82</td>
</tr>
<tr>
<td>TN</td>
<td>8.99</td>
<td>$\text{SO}_4^{2-}$</td>
<td>1.56</td>
</tr>
</tbody>
</table>
content (x) of formic acid are linearly regressed. The regression equation is \( y = 555.4x - 300.2 \), and the linear correlation coefficient is 0.9997.

**Determination of formic acid content.** The peak area of formic acid was measured by taking 3 parallel samples of the condensate, and the content of formic acid was determined between the peak area and the standard curve. The relative average deviation was calculated. Results are shown in Table 3.

Seen from Table 3, the content of formic acid in the condensate is 3.2 mg·L\(^{-1}\) and the relative average deviations is 2.1%, 2.8%, and 0.6%, respectively, which is consistent with the results by ion chromatography.

**Spiked recoveries of formic acid.** The content of formic acid measured by HPLC was 3.2 mg·L\(^{-1}\). In order to verify the content accuracy analysis of formic acid in the condensate, the spiked recoveries of formic acid were determined and results are shown in Table 4.

As shown in Table 4, the spiked recoveries of formic acid in the condensate are in the range of 96.2–109.6%, within the confidence interval of 90–110%. It indicates that the content analysis of formic acid in the condensate is reliable by HPLC.

**Analysis of alcohols in the condensate**

The content of formic acid in the condensate is 3.2 mg·L\(^{-1}\), which is about 0.85 mg·L\(^{-1}\) TOC. However, the TOC of the condensate is 17.81 mg·L\(^{-1}\) and formic acid only accounts for 5%, which indicates the presence of other small-molecule organics. Therefore, the trace alcohols in the condensate were analyzed by GC.

**Qualitative analysis**

GC chromatograms of condensate, and mixed standard solutions of methanol (8.0 mg·L\(^{-1}\)) and ethanol (4.0 mg·L\(^{-1}\)) were determined and are shown in Figure 3.

As shown in Figure 3, the retention time of methanol and ethanol is 2.4 and 2.6 min, respectively. The trace organics in the condensate are in the same peak positions as methanol and ethanol, and the content of methanol is significantly higher than that of ethanol.

**Quantitative analysis of methanol and ethanol**

**Standard curves of methanol and ethanol.** Referring to GB/T602-2002, standard solutions of methanol (8.0, 16.0, 32.0, 40.0 and 80.0 mg·L\(^{-1}\)) and ethanol (0.8, 1.0, 2.0, 4.0 and 8.0 mg·L\(^{-1}\)) were prepared. The standard curves of methanol and ethanol were measured. The relationship between \( y_1 \) (peak area of methanol) and \( x_1 \) (content of methanol), \( y_2 \) (peak area of ethanol) and \( x_2 \) (content of ethanol) are shown in Figure 4(a) and 4(b).

As shown in Figure 4(a), when the content of methanol is in the range of 8–80 mg·L\(^{-1}\), the peak area \( y_1 \) and the content of methanol \( x_1 \) are linearly regressed. The regression equation of methanol is \( y_1 = 62.42x_1 + 181.96 \), and the linear correlation coefficients of methanol is 0.9996. From Figure 4(b), the content of ethanol is in the range of 0.8–8.0 mg·L\(^{-1}\), the regression equation of ethanol is \( y_2 = 31.68x_2 - 1.02 \), and the linear correlation coefficient of ethanol is 0.9992. The results of methanol and ethanol measured by GC have a good correlation.

---

**Table 3** | Content of formic acid in the condensate determined by HPLC

<table>
<thead>
<tr>
<th>Parallel test</th>
<th>Peak area, mAU·min</th>
<th>Content, mg·L(^{-1})</th>
<th>Relative average deviation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,515</td>
<td>3.3</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>1,427</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>1,488</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Average</td>
<td>1,476</td>
<td>3.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Table 4** | Determination for spiked recoveries of formic acid in condensate by HPLC

<table>
<thead>
<tr>
<th>Number</th>
<th>( C_0 ), mg·L(^{-1})</th>
<th>( C_2 ), mg·L(^{-1})</th>
<th>( P ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>2.7</td>
<td>106.1</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>3.8</td>
<td>109.6</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>5.5</td>
<td>96.2</td>
</tr>
</tbody>
</table>

**Figure 3** | GC chromatograms of condensate and standard mixture solution.
Content determination of methanol and ethanol. The peak areas of methanol and ethanol were measured by taking three parallel samples of the condensate, and the contents of methanol and ethanol were determined between the peak area and the standard curve. The relative average deviation was calculated and results are shown in Table 5.

The average content of methanol and ethanol is 41.4 and 2.1 mg·L$^{-1}$ (in Table 5), respectively. The relative average deviations for the content of methanol and ethanol are within 2%, indicating that the determinations of methanol and ethanol in the condensate by GC have good repeatability.

Spiked recoveries of methanol and ethanol. In order to verify the determination accuracy of methanol and ethanol in the condensate, the spiked recoveries of methanol and ethanol were studied. The results are shown in Table 6.

The spiked recoveries of the methanol and ethanol in the condensate determined by GC are in the range of 94.0–106.9% and 90.7–105.7%, respectively, both in the range of 90–110%, which indicate that the measurement results are reliable.

In summary, the content of formic acid, methanol and ethanol in the condensate is 3.2, 41.4 and 2.1 mg·L$^{-1}$, respectively. The theoretical value of TOC from formic acid, methanol and ethanol is 17.48 mg·L$^{-1}$ (calculated for organic carbon), which is close to the experimental value of TOC (17.81 mg·L$^{-1}$). The contents of formic acid, methanol and ethanol measured by HPLC and GC are reliable.

### Table 5 | Contents of methanol and ethanol in the condensate measured by GC

<table>
<thead>
<tr>
<th>Parallel test</th>
<th>Peak area, μV·min</th>
<th>Content, mg·L$^{-1}$</th>
<th>Relative average deviation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
<td>Ethanol</td>
<td>Methanol</td>
</tr>
<tr>
<td>1</td>
<td>2,761</td>
<td>66</td>
<td>41.3</td>
</tr>
<tr>
<td>2</td>
<td>2,723</td>
<td>64</td>
<td>40.7</td>
</tr>
<tr>
<td>3</td>
<td>2,814</td>
<td>65</td>
<td>42.2</td>
</tr>
<tr>
<td>Average</td>
<td>2,766</td>
<td>65</td>
<td>41.4</td>
</tr>
</tbody>
</table>

### Table 6 | Spiked recoveries of methanol and ethanol in condensate measured by GC

<table>
<thead>
<tr>
<th>Number</th>
<th>$C_0$, mg·L$^{-1}$</th>
<th>$C_p$, mg·L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Ethanol</td>
</tr>
<tr>
<td>1</td>
<td>16.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>32.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>40.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 4 | Standard curves of (a) methanol and (b) ethanol measured by GC.
Correlation analysis between organics and COD in the condensate

In order to determine the main source of COD in the condensate, a correlation analysis between organics and COD was carried out. In this article, the COD corresponding to the trace organics is the amount of oxygen required when the trace organics are completely oxidized to CO₂ and H₂O. Taking the general form of organics as an example, the theoretical value of COD was calculated by Equations (2) and (3).

\[ C_{x}H_{y}O_{z} + \left( \frac{2x+y}{2} - z \right)O = xCO_{2} + \frac{y}{2}H_{2}O \]  \hspace{1cm} (2)

\[ C_{COD} = \frac{C_{x}H_{y}O_{z} \times M_{O}}{M_{organic}} \]  \hspace{1cm} (3)

where \( C_{x}H_{y}O_{z} \) is the general form of organics, \( C_{x}H_{y}O_{z} \) (mg·L⁻¹) is the content of organics in the condensate, \( M_{O} \) is the molar mass of oxygen consumed when organics are absolutely converted to CO₂ and H₂O, \( M_{organic} \) is the relative molecular weight of the organics, \( C_{COD} \) (mg·L⁻¹) is the theoretical value of COD.

The COD of the condensate is 74.1 mg·L⁻¹, and the trace organics are mainly methanol, ethanol and formic acid. The correlation of organics and COD are shown in Table 7.

The contents of methanol, ethanol and formic acid are 41.4, 2.1 and 3.2 mg·L⁻¹, respectively. Theoretical value of COD calculated based on Equations (2) and (3) is 67.6 mg·L⁻¹, which is 91.2% of the experimental value of COD (74.1 mg·L⁻¹). Among all organics, the contribution rate of methanol to COD is 83.8%. The experimental value of the COD is slightly higher than the theoretical one, which is related to the error caused by trace acetic acid (0.17 mg·L⁻¹) in the condensate. At the same time, Cl⁻ can easily be oxidized to Cl₂ using potassium dichromate as the oxidant for COD. The content of Cl⁻ in the condensate is 1.42 mg·L⁻¹, which is ~0.52 mg·L⁻¹ COD (theoretical value of COD generated by 1 mg Cl⁻ is 0.23 mg). I⁻ is the same family as Cl⁻, and the electronegativity is less than that of Cl⁻, so it also can be oxidized to I₂ during the digestion. The content of I⁻ in the condensate is 7.82 mg·L⁻¹ with the corresponding COD of 1.78 mg·L⁻¹. In addition, the ammonia nitrogen in the condensate is 0.18 mg·L⁻¹ (about 0.22 mg·L⁻¹ NH₃), which is ~0.99 mg·L⁻¹ COD (theoretical value of COD generated by 1 mg NH₃ is 4.57 mg). The total theoretical value of COD from organics and the anions in the condensate is up to 70.9 mg·L⁻¹, which is close to the measurement value of COD (74.1 mg·L⁻¹).

The correlation analysis of organics and COD indicates that methanol is the main source of COD (83.8%). Table 8 shows the relationship between the COD condensate and the content of methanol in the condensate, which provides a reference for reducing the COD and developing a reasonable adsorption and purification process of the condensate.

As shown in Table 8, the content of methanol in the condensate is linearly correlated with COD. When the content of methanol in the condensate dropped from 41.4 to 2.1 mg·L⁻¹, the COD of the condensate correspondingly decreased from 74.1 to 4.7 mg·L⁻¹. This shows that the purified condensate could be reused in the circulating water system of the hydrogen production plant, and removing the trace methanol to lower the COD is the key step. The results of this paper might provide basic data for the development of the adsorbent and the purification process of the condensate.

**CONCLUSIONS**

(1) The content of methanol (GC), ethanol (GC) and formic acid (HPLC) in the condensate is 41.4, 2.1 and 3.2 mg·L⁻¹, respectively. The spiked recoveries of three organics are 96.1%, 100.2% and 105.9%, respectively. The determination methods and the data are reliable.

(2) Theoretical COD value of methanol, ethanol and formic acid in the condensate is 67.6 mg·L⁻¹, which is 91.2% of the measured value of COD. Methanol is the main source of COD in the condensate and the contribution rate of methanol to COD is 83.8%. In addition, the contents of Cl⁻, I⁻ and ammonia nitrogen in the condensate can affect the determination results of COD.
(3) The decrease of methanol content can significantly reduce COD in the condensate. The results can provide research direction and basic data for the development of the adsorbent and adsorption purification process of the condensate.

ACKNOWLEDGEMENTS

This work was supported by the Innovative Research Group Project of the National Natural Science Foundation of China (No. 51476074); and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Sinopec Co. Ltd (No. 30600000-18-ZC0607-0006).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Chen, L. & Jia, J. 2013 The different opinions of chloride ion’s interference in the process of national standard method to determine the CODCr. Science and Technology Information 1, 189–190. doi:10.3969/j.issn.1001-9960.2013.01.139.


Wang, X. 2008 Study on Treatment and Reuse of Condensate Wastewater. Masters dissertation, Nanjing University of Science and Technology, Nanjing, China.


