Parameter setting for peak fitting method in XPS analysis of nitrogen in sewage sludge

Z J Tang, P Fang*, J H Huang, P Y Zhong
South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655, PR China

*fangping@scies.org

Abstract. Thermal decomposition method is regarded as an important route to treat increasing sewage sludge, while the high content of N causes serious nitrogen related problems, then figuring out the existing form and content of nitrogen of sewage sludge become essential. In this study, XPSpeak 4.1 was used to investigate the functional forms of nitrogen in sewage sludge, peak fitting method was adopted and the best-optimized parameters were determined. According to the result, the N1s spectra curve can be resolved into 5 peaks: pyridine-N (398.7±0.4eV), pyrrole-N(400.5±0.3eV), protein-N(400.4eV), ammonium-N(401.1±0.3eV) and nitrogen oxide-N(403.5±0.5eV). Based on the the experimental data obtained from elemental analysis and spectrophotometry method, the optimum parameters of curve fitting method were decided: background type: Tougaard, FWHM 1.2, 50% Lorentzian-Gaussian. XPS methods can be used as a practical tool to analysis the nitrogen functional groups of sewage sludge, which can reflect the real content of nitrogen of different forms.

1. Introduction
Sewage sludge is an unavoidable residual matter from waste water. Nowadays, the thermal decomposition method is widely used as a fast and efficient route to treat sewage sludge. However, large majority of sewage sludge contains considerable amount of nitrogen (2.4-9.0%) [1,2], then figuring out the existing form and content of nitrogen of sewage sludge become essential.

As a mature and convenient method, XPS is widely used in analysis the elemental content of solid samples, such as coal, soil, etc [3,4]. Peak fitting softwares such as XPSpeak 4.1, Casa XPS and Thermo Advantage, etc. are widely used in analysis the existing form and content of nitrogen. The parameters such as peak position, background type (BT), full width at half maximum (FWHM) and %Lorentzian-Gussian (%L-G) are essential in the determination of N-containing component content, while few studies focus on these issues.

Therefore, in this study, based on the data obtained from classic spectrophotometry methods, the optimum peak fitting parameters of XPS curve fitting method were determined by using XPSpeak 4.1 software.

2. Materials and methods

2.1. Preparation and property of raw sludge sample
Sewage sludge used in this study was dewatered sludge which came from a municipal sewage treatment plant in Guangzhou, China. After natural drying in open area for 3-5 days, the sludge was milled below
75μm, and then put into constant temperature and constant humidity box (T: 20 °C, H: 60%) before use. The compositions of the sludge sample are shown in Table 1.

### Table 1. Proximate, ultimate analysis and chemical compositions of sludge sample.

| Proximate analysis (wt.%) | Ultimate analysis (wt.%, dry base) |
|--------------------------|-----------------------------------|
| ω(Mt) | ω(M ad) | ω(A ad) | ω(V ad) | ω(FC ad) | ω(C) | ω(H) | ω(N) | ω(S) | ω(O) |
| 77.22 | 8.63 | 49.83 | 33.98 | 7.56 | 25.30 | 4.06 | 6.80 | 1.20 | 18.59 |

| Chemical compositions(wt.%, dry base) |
|---------------------------------------|
| SiO₂ | Al₂O₃ | Fe₂O₃ | P₂O₅ | CaO | K₂O | SO₃ | TiO₃ | MgO | ZnO |
| 24.42 | 18.66 | 17.24 | 14.10 | 9.08 | 6.02 | 3.25 | 3.18 | 1.28 | 0.85 |

#### 2.2. Experimental methods and devices

In this study, the content of total nitrogen was detected by elemental analyzer (Eurovector, EA3000). Protein-N(Pr-N), ammonium-N(A-N), and nitrate/nitrite-N were determined by using US-VIS spectrophotometer (HACH, DR5000), extraction reagents and standard references are shown in Table 2. Heterocycle-N(He-N) and nitrogen oxide-N(NOx-N) were calculated according to equation (1) and equation (2) respectively.

### Table 2. Detection methods of different forms of nitrogen

| No. | Analysis item | Extraction reagent | Standard | Standard No. |
|-----|---------------|--------------------|----------|--------------|
| 1   | Pr-N          | /                  | National food safety standard Determination of protein in foods | GB5009.5-2010 |
| 2   | A-N           | 2 mol/L KCl        | Water quality-Determination of Ammonium - Nessler’s Reagent Spectrophotometry | HJ535-2009 |
| 3   | NOx-N         | saturated solution of CaSO₄ | Water quality-Determination of nitrate - Spectrophotometric method with phenol disulfonic acid(NO₃⁻-N) | GB7480-87 |

\[ \text{He-N} (%) = (T-N) - (Pr-N) - (NH}_4^+ - N) - (NO}_3^- - N) - (NO}_2^- - N) (\%)
\]

\[ \text{NOx-N} (\%) = (NO}_3^- - N) + (NO}_2^- - N) (\%)
\]

#### 3. Results and Discussions

Results of the concentrations of different nitrogen functional groups determined by using traditional spectrophotometry methods are shown in Table 3.

### Table 3. Existing form and content of nitrogen of sludge sample

| Organic-N | Inorganic-N |
|-----------|-------------|
| Pr-N      | He-N        | A-N | NO₃⁻-N | NO₂⁻-N |
| %N | %T | %N | %T | %N | %T | %N | %T |
| 64.12 | 4.36 | 32.94 | 2.24 | 2.21 | 0.15 | 0.74 | 0.05 | 0.02 | 0.00 |

As can be seen in Table 3, the forms of nitrogen can mainly be classified into organic-N and inorganic-N. The former one was dominant, which account for 95.06% of total nitrogen. The type of protein-N took the highest part among all the nitrogen containing components, and ammonium-N accounted for the largest proportion of inorganic nitrogen.
The N1s spectra peak fitting curves with different peak fitting parameters are shown in Figure 1. According to model compound data and references [3,5,6], the N1s spectra curve can mainly be resolved into 5 peaks: pyridine-N (398.7±0.4 eV, N-6), pyrrole-N (400.5±0.3 eV, N-5), protein-N (400.4 eV, Pr-N), ammonium-N (401.1±0.3 eV, A-N) and nitrogen oxide-N (403.5±0.5 eV, NOx-N). The integral values of peak areas were calculated and the relative contents of different N-containing compounds were obtained according to equation (3) and equation (4). The results are shown in Table 4.

![Figure 1](image-url)

Figure 1. N1s peaks for sewage sludge with different curve fitting parameters

Table 4. Existing form and content of nitrogen of sludge sample

| Organic-N | Inorganic-N |
|-----------|-------------|
| Pr-N      | N-6         | N-5 | A-N | NOx-N |
| %N        | %T          | %N  | %T  | %N   | %T   | %N  | %T   |
| A         | 21.61       | 1.42| 59.99| 3.95| 18.4 | 1.21| 0.00| 0.00| 0.00 |
| B         | 44.87       | 2.96| 36.06| 2.38| 0.00| 15.00| 0.99| 4.07| 0.27 |
| C         | 53.56       | 3.53| 27.65| 1.82| 0.00| 16.32| 1.08| 2.47| 0.16 |
| D         | 65.07       | 4.29| 21.67| 1.43| 10.22| 0.67| 3.03| 0.20| 0.00| 0.00 |

\[
\%N(\%) = \frac{\text{area of fitting peak}}{\text{total area of fitting peaks}} \times 100\% \quad (3)
\]

\[
\%T(\%) = \%N \times \text{the content of nitrogen in sludge}/100(\%) \quad (4)
\]
Comparing the results in Table 4 and Table 3, it can be found that the total nitrogen content of sewage sludge detected by XPS method was 6.59%, which was close to the N-content analyzed by elemental analyzer. As X-ray photoelectron can only detect the elemental concentration on the sample surface, the close values of the two methods proved the homogeneity of the sewage sample. The parameters selection was essential in XPS curve fitting method. Comparing the four sets of parameters, it can be found, when the background type was Tougaard, FWHM was 1.2, %Lorentzian-Gaussian was chose to be 50, the contents of N-containing compounds in sludge sample analyzed by XPS curve fitting method were in good similarity to the real ones detected by spectrophotometry. The protein-N and ammonium-N content of two methods were close, the values of heterocycle-N calculated according to equation (1) and simulated ones by peak fitting method were identical, which means the heterocycle-N was mainly in the form of pyridine-N and pyrrole-N. The peak area of nitrates and nitrites nitrogen were pretty small which can’t be calculated by XPS curve fitting method, while using classical spectrophotometry, the relative content of nitrate-N and nitrite-N both can be detected.

In a word, XPS curve fitting methods can be used as a practical tool to analysis the content of N-containing components in sewage sludge.

4. Conclusion
- The combination of elemental analysis and spectrophotometry and the method of XPS curve fitting can both be used as a tool to determine the nitrogen distribution in sewage sludge.
- The forms of nitrogen can mainly be divided into organic-N (protein-N and heterocycle-N) and inorganic-N (ammonium-N and nitrate/nitrite-N), the former one was dominant, which occupied 95.06% of total nitrogen.
- The N1s spectra curve can be resolved into 5 peaks: pyridine-N (398.7±0.4eV), pyrrole-N(400.5±0.3eV), protein-N(400.4eV), ammonium-N(401.1±0.3eV) and nitrogen oxide-N(403.5±0.5eV).
- Based on the experiment data obtained from elemental analysis and spectrophotometry method, the optimum parameters of curve fitting method were as below: background type: Tougaard, FWHM 1.2, 50% Lorentzian-Gaussian.
- XPS methods can be used as a practical tool to analysis the nitrogen functional groups of sewage sludge, which can reflect the real content of nitrogen of different forms.

Acknowledgements
This work was financially supported by National Natural Science Foundation of China (51778264), Guangdong Natural Science Foundation (2015A030310344), Program for the Young Top-notch Talents of Guangdong province (2016TQ03Z576), Pearl River S&T Nova Program of Guangzhou (201610010150), and Special Funds for Research from the Environmental Charity Project (Grant PM-zx703-201701-050).

References
[1] Tyagi V K and Lo S L 2013 Microwave irradiation: a sustainable way for sludge treatment and resource recovery (Renewable & Sustainable Energy) vol 18 pp 288-305.
[2] Tian Y, Zhang J and Zuo W 2013 Nitrogen conversion in relation to NH3 and HCN during microwave pyrolysis of sewage sludge (Environmental Science & Technology) vol 47 pp 3498-3505.
[3] Wojtowicz M A, Pels J R and Moulijn J A 1995 The fate of nitrogen functionalities in coal during pyrolysis and combustion (Fuel) vol 74 pp 507-516.
[4] Gorbuty M L and Kelemen S R 2001 Characterization and reactivity of organically bound sulfur and nitrogen fossil fuel (Fuel Process Technology) vol 71 pp 71-78.
[5] Gong B, Buckley A N and Lamb R N 1999 XPS determination of the forms of nitrogen in coal pyrolysis chars (Surface & Interface Analysis) vol 28 pp 126-130.
[6] Zhang Y C, Zhang J and Sheng C D 2011 X-ray photoelectron spectroscopy (XPS) investigation
of nitrogen functionalities during coal char combustion in O₂/CO₂ and O₂/Ar atmospheres (Energy Fuels) vol 25 pp 240-245.