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To cite this article: Tao Wan *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **295** 042088

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Detection of Total Corrosive Sulfur in Transformer Oil

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Abstract. The quantitative analysis methods of the total corrosive sulfur (TCS) in transformer oils were realized using copper powder corroding technique. In this technique, excess copper powder reacted with insulating oils at 150°C for 12 hours to form corrosion product (Cu₂S). Then, Cu₂S was oxidized to CuSO₄²⁻, and finally dissolved to sulfate solution. There are three methods to test the amount of TCS. SO₄²⁻ solution tested by ion chromatography (IC) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Moreover, adopted ICP to test total sulfur (TS) in oils before and after corrosion reaction, and the difference value is the content of TCS. Comparing with these methods, it was found that ICP detection of total sulfur (TS) in oils could achieve excellent linearity. The correlation coefficients is $R^2 \geq 0.999$, and the recovery rate is 98.4%~103.4%.

1. Introduction

Many transformer faults happened due to corrosive sulfur have been reported and corrosive sulfur compounds significantly affect on long term operation of transformer oil was recognized [1-3]. The amount of total sulfur (TS) in a typical insulating oil is about 0.001~0.5%, including elemental sulfur, inorganic sulfur compounds and organic sulfur compounds [4-5]. However, not all the sulfides are corrosive, and different sulfur compounds have different corrosivity toward copper in insulating oils. The corrosive sulfurs attack copper winding to form conductive substance (Cu₂S) and migrate to the insulation oil-paper. Slowly insulation weakened, and eventually lead to transformer breakdown cases [6-7]. According to ASTM D3487, DIN 51353 and IEC 62535, corrosive or non-corrosive of insulating oils towards copper are qualitatively determined with perception of color [8-9]. Furthermore, The qualitative test methods would give "false negative" test result for corrosive sulfur in insulating oils that contained metal passivator additive. The quantitative detection of corrosive sulfur can directly and accurately determine the corrosive sulfur concentration in insulating oils, and better illustrate the corrosion degree of the oil to transformers [10-11]. At present, the quantification method of total corrosive sulfur (TCS) in insulating oils by using ion chromatography (IC) has been reported [12]. However, the detection of sulfate may be interfered with by nitrate in solution, especially at trace concentration.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a preferred instrument for elemental analysis and has been used to analysis additive elements in used lubricating oils [13-14]. The ICP theory is that sample solution enters the atomizer through peristaltic pump and forms aerosol, which is introduced into the plasma by carrier gas. Then the compositions of aerosol are atomized,



ionized and excited, emitting characteristic spectra of contained elements. The qualitative and quantitative analysis can be carried out according to different elements different possess and intensity of characteristic spectral wavelength.

In this paper, alternative ICP methods were proposed to overcome the interference of nitrate in solution and avoid complex process of copper powder oxidation.

2. Experimental procedure

2.1. Material and instrument

Refined base oil: total sulfur content 15mg/kg and non-corrosive, China National Petroleum Corporation. Copper powder: purity 99.5%, good dispersion. Dibenzyl disulfide (DBDS): purity 99.99%, TCI Shanghai Development Corporation. Octane, Pentane and KNO_3 solid from Sinopharm Reagent Co., Ltd.. Petroleum ether: pure, ACROS Organics. Methyl silicone oil: Rongcheng Silicone Materials Co., Ltd. ICAP 6300 inductively coupled atomic spectrometer: Thermo Fisher Scientific Co. Ltd., equipped with an organic injection system. ICS-5000 Ion Chromatograph: Thermo Fisher Scientific Co. Ltd..

2.2. Preparing sample oil and CuSO_4 solution

Stock sample oil was prepared by dissolving DBDS in refined insulating oil with TCS content of 1000 mg/kg. A set of the calibration standard oils of TCS concentration from 0 to 591 mg/kg were prepared by diluting the stock sample oil and store them in a brown bottle.

The oil sample ($10\text{g}\pm 0.5\text{g}$) and copper powder ($3\text{g}\pm 0.1\text{g}$) were placed in a glass vial. Then, The vial was fill with nitrogen, and tighten the cap. After reacting with constantly steering at 150°C for 12 hours, The vial was slowly poured out the oil and prevented copper powder discharge. Washed, dried, cooled, and reacted with KNO_3 solid at 350°C for 2 hours until the copper powder became completely black. Dissolved oxidation products CuSO_4^{2-} with deionized water by heating at 120°C for $15\sim 20\text{min}$, and then filter the solution into a bottle. Washed twice with deionized water, transferred solution to the same bottle, and finally set the volume to 20 mL.

2.3. Analytical methods for TCS

There are three methods to detect the amount of TCS. IC detection of SO_4^{2-} solution, ICP detection SO_4^{2-} solution and ICP detection the difference value of TS in the oil sample before and after reaction.

2.3.1. IC detection solution. Take 100 μL prepared solution diluted to 100 mL with deionized water, and then 250 μL of the diluted solution was filtered through a 0.22 μm filter. Using 2.2 mmol Na_2CO_3 with 2.8 mmol NaHCO_3 as the mobile phase of the ion chromatography, and the flow rate was 1.8mL/min.

2.3.2. ICP detection solution. The prepared solution was diluted with deionized water, and tested with emission characteristic spectral wavelength at 1807nm, 1820nm and 1826nm. Cooling gas flow rate was 12.0 L/min. Auxiliary gas flow rate was 1.0 L/min. Atomizing gas flow rate was 0.50 L/min. RF power was 1150 W.

2.3.3. ICP detection oils. The oils sample before and after reaction are diluted with petroleum ether, respectively. Sulfur content was detected with emission characteristic spectral wavelength at 1807nm, 1820nm and 1826nm. Cooling gas flow was 12.0 L/min. Auxiliary gas flow was 1.0 L/min. Atomizing gas flow was 0.75 L/min. RF power was 1350 W;

2.4. Oil sample analysis

After the copper powder corrosion reaction and SO_4^{2-} generation such as section 2.2, the amount of TCS in the insulating oil was determined by the three methods described in the section 2.3.

3. Results

3.1. Analysis of calibration standard samples

To obtain the unary linear regression between the amount of TCS in transformer oils and ion chromatography peak height of sulfate, 5 types of calibration standard oils (0, 10, 90, 285 and 591 mg/kg) were prepared in lab and the corresponding standard solution were tested by IC after corrosion reaction. Based on the least squares method, the fitting result is presented in Figure 1. Result shows a good linear relationship, and the goodness of fit is $R^2 = 0.99503$.

The regression equation is:

$$y=0.07973+0.00716x \tag{1}$$

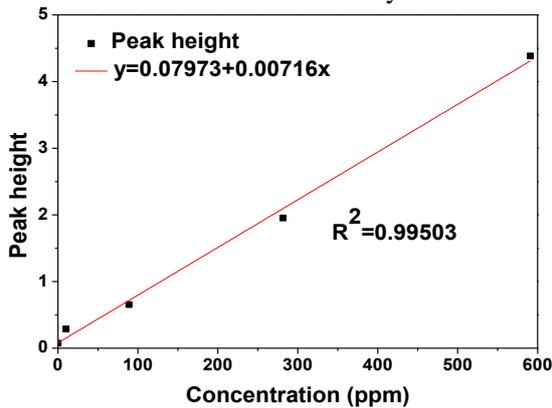


Figure 1. Calibration curve of IC detection standard solution

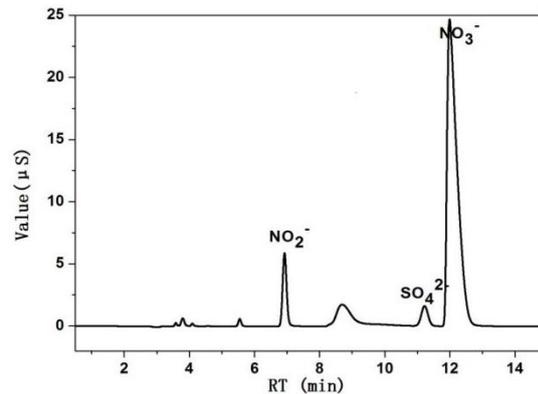


Figure 2. The ion chromatogram of the calibration TCS as sulfate in solution

Figure 2 shows the ion chromatography of the solution obtained by calibration standard oil (10 mg/kg). In copper powder corroding technique, the excess KNO_3 was used to ensure copper sulfide was fully oxidized to sulfate. The SO_4^{2-} in aqueous solution is much smaller than NO_3^- and NO_2^- , that may cause IC detection results to be disrupted.

In order to verify the reliability of IC method, the above standard solutions were tested with ICP. Figure 3 shows the calibration curve with a better linear relationship for TCS by ICP test SO_4^{2-} solution compare to IC method. The goodness of fit is $R^2 = 0.99989$ and the regression equation is:

$$y=187.87086+72.58255x \tag{2}$$

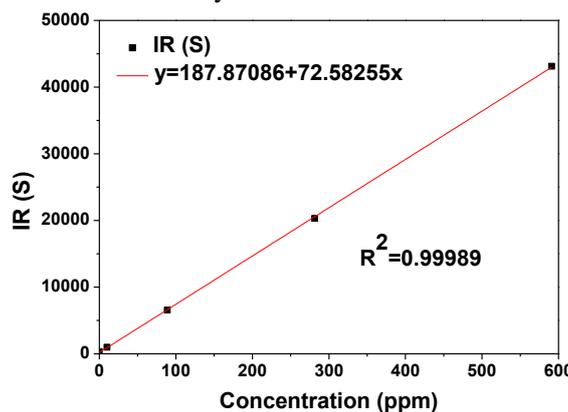


Figure 3. Calibration curve of ICP detection TCS as sulfate in solution

In addition, directly test the 5 types of calibration standard oils (0, 10, 90, 285 and 591 mg/kg) with ICP, and obtained a linear relationship between the amount of sulfur and the response values of ICP. Figure 4 shows the calibration curve follow with the best linear relationship in the three test method. The goodness of fit is $R^2 = 0.99994$ and the regression equation is:

$$y=927.64291+21.52061x \tag{3}$$

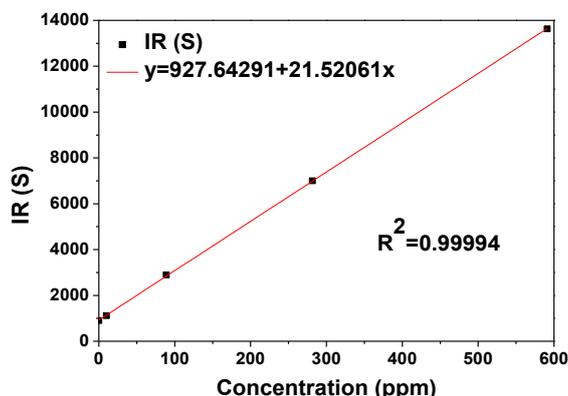


Figure 4. Calibration curve of TCS by ICP directly test oil sample

3.2. Insulating oils analysis

The oil samples in service were tested by these three methods, respectively. As shown in Table 1, for the same oil sample, the values of the ICP detection solution and oil are similar, while the value of the IC detection solution is smaller than ICP detection results.

Table 1. IC and ICP test results for running oil samples

Oils sample	IC solution/(mg/kg)	ICP solution/(mg/kg)	ICP oil/(mg/kg)
1	23.30	31.98	33.90
2	5.81	8.02	8.80
3	44.04	49.02	51.46

In order to verify whether the complex process of copper powder influences the determination of the sample and interfere with other substrates in the detection process, a standard recovery test was conducted for the running oil sample 1. In the recovery test, the adding standard content of corrosive sulfur was 19.8, 39.3, 56.9, 76.4, 118 and 199 mg/kg, respectively. The oil added with corrosive sulfur was detected by three methods described in section 2.3. Standard recovery results of these three methods are shown in Table 2, 3 and 4. As shown in Table 2, the recovery rate of IC method detection TCS as sulfate in solution is 96.1% ~ 124.3%. It found that recovery rate of this method at low concentration had a great deviation. It may be due to IC detection process with other ion interference. As shown in Table 3, the recovery rate of ICP detection solution is in range of 95.8% ~ 105.4%. As shown in Table 4, the recovery rate of ICP detection oils is in range of 98.5% ~ 103.4%. The results show that ICP test solution and oil both have good recovery rate. Directly on the oil samples for testing, reducing the complexity of copper powder process, effectively avoiding error in the sample processing. ICP directly tests transformer oils before and after reaction is the best in these methods.

Table 2. A standard recovery test of IC detection solution

Oil Number	Original /ppm	Add content /ppm	Detection value /ppm	Recovery rate /%
1	18.64	19.8	43.26	124.3%
2	18.64	39.3	64.82	117.5%
3	18.64	56.9	84.93	116.5%
4	18.64	76.4	92.06	96.1%
5	18.64	118	139.7	102.5%
6	18.64	199	254.2	118.3%

Table 3. A standard recovery test of ICP detection solution

Oil Number	Original /ppm	Add content /ppm	Detection value /ppm	Recovery rate /%
1	25.56	19.8	44.95	97.9
2	25.56	39.3	67.92	105.2
3	25.56	56.9	85.55	105.4
4	25.56	76.4	102.6	100.8
5	25.56	118	138.6	95.8
6	25.56	199	222.8	99.1

Table 4. A standard recovery test of ICP detection oils

Oil Number	Original /ppm	Add content /ppm	Detection value /ppm	Recovery rate /%
1	27.12	19.8	47.60	103.4
2	27.12	39.3	65.88	98.6
3	27.12	56.9	83.12	98.4
4	27.12	76.4	104.0	100.6
5	27.12	118	148.4	102.7
6	27.17	199	231.0	102.4

4. conclusions

This work clearly showed the potential of ICP-AES use for quantitative analysis of TCS in transformer oil. Using ICP to detect TCS as sulfate in solution could avoid the interference of nitrate in solution. Using ICP to directly test oil before and after reaction can reduce the error in copper powder processing. The good relationship between TCS content and the response values of these three methods, and the relationship of ICP directly tests oil before and after reaction could achieve 0.99994. Moreover, the standard recovery test was performed on running oil. It found that the standard recovery of ICP detection oils before and after reaction was in range of 98.5% ~ 103.4%. This indicated that the ICP method for detecting TCS in transformer oil could be a promising method in quantitative corrosive sulfur test.

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