Pretreatment in the Determination of Trace Copper and Iron in Transformer Oil

Qinqin Liang¹, Zongchang Luo¹
¹Guangxi Power Grid Electric Power Research Institute, Nanning 530023, China
Corresponding author’s e-mail: liang_qq.sy@gx.csg.cn

Abstract: Comparative trace copper and iron analysis of unused and running transformer oil is performed by ICP-MS with pretreatment by ashing, acid dissolution and direct injection method. The advantages and drawbacks of each of the listed methods are discussed. The direct injection method is so simple and time-consuming that can realize accurate determination of copper in oil, while it is not suitable for determination of iron in used transformer oil. Although limited by availability of equipment, acid dissolution method has good accuracy and reproducibility for the determination of transformer oil in all states.

1. Introduction
With the development of power transmission and conversion technology, compact insulation structure is adopted in the design and manufacture of transformers with high-voltage and large capacity. Transformer oil plays an important role in ensuring safe and reliable operation of transformers by its good insulation performance. However, large numbers of impurities are introduced into the transformer oil in the process of manufacture and operation of transformer inevitably due to various factors, some of which are conductive particles that lead to corona discharge when their surface field strength produced by the external electric field exceeds the breakdown voltage of transformer oil[1]. More seriously, when larger conductive particles containing metal elements like iron and copper are close to bare electrodes[2], local field strength between them increases greatly and results in partial discharge accompanied with bubbles which further enhances partial discharge and decreases the breakdown voltage of transformer oil. Therefore, contents of trace copper and iron in transformer oil are not only an indicator for evaluating performance of transformer oil in service, but also accurately reflect the running state of transformer, which is also crucial for the maintenance and evaluation of working performance of transformer.

High-precision analytical instruments are widely used in evaluation of transformer oil aiming to establish an analysis method that can quickly and accurately estimate copper and iron with low-contents[3]. To be accepted, the limiting step in the elemental analysis of transformer oil is sample pretreatment that should be time-efficient, productive and also ensure the minimization of element losses as volatile species and the minimal level of sample contamination by operation. The present work introduces and compares different pretreatment methods for determination of trace copper and iron in transformer oil by ICP-MS.
2. Experimental Section

2.1. Reagents
Nitric acid, Merck(HPLC Grade); hydrochloric acid, Merck(HPLC Grade); hydrogen peroxide, Sinopharm Chemical Reagent Co., Ltd(AR); jet fuel, CONOSTAN; oil analysis standards, CONOSTAN.

2.2. Instrument configurations
The experiments were performed using a Thermo-fisher iCAP-Q ICP-MS which parameters were adjusted to attain a higher sensitivity and reduce isobaric interferences as Table 1.

| Parameter          | Value             |
|--------------------|-------------------|
| Mode               | CCT               |
| Plasma gas flow    | 14 L/min          |
| CCT gas flow       | 8.5 L/min         |
| Auxiliary gas flow | 0.8 L/min         |
| Carrier gas flow   | 1.1 L/min         |
| Atomizer           | Concentric        |
| Atomization chamber| Quartz            |
| Sampling interval  | 45s               |
| Quantitative method| External standard method |
| Elements           | $^{63}$Cu $^{57}$Fe |

2.3. Pretreatment Method

Ashing method. Weighed 5g oil sample accurately to 0.001g and poured into a quartz beaker, then placed beaker on an infrared heating plate which is set at 350℃. After oil sample was evaporated to dryness for heating more than 4 hours, slowly ashed it on an adjustable electric furnace for 3 hours. After cooling, added 10ml of (1+1) hydrochloric acid into beaker and heated at low temperature until 2-3ml of the solution remained. Finally used (2+98) nitric acid to dilute remained solution to 50ml as sample to be determined.

Acid dissolution method. Mixed acid solution was composed of 7.5% nitric acid and 22.5% hydrochloric acid. 2ml oil sample was weighed (accurate to 0.001g) and injected into a 50ml flask. Added 16 ml mixed acid solution and 4ml hydrogen peroxide into flask and then heated solution to boiling after putting some glass beads into flask. After boiling for 35 minutes, stopped heating and let flask stand for 10 minutes. Then transferred solution in flask into a separating funnel to delaminate acid solution and oil sample. Took lower solution 5ml and diluted to 10ml with deionized water as sample to be determined.

Direct injection method. Weighed about 1g (accurate to 0.001g) of oil and diluted to 10g with jet fuel by 20-minute ultrasonic treatment to ensure that the sample to be determined was fully mixed.

3. Results and discussion
The contents of copper and iron was quantified by External standard analysis. Samples pretreated by ashing method and acid dissolution method were both inorganic solution at last and can be quantified by a same inorganic calibration plot evaluated by 0-50ppb inorganic standard solution based on 3% nitric acid solution[4]. Meanwhile, organic calibration plot was evaluated by organic standard solution by dilution of CONOSTAN oil analysis standards with jet fuel. The results were shown in Figure 1. Due to high sensitivity and stability of ICP-MS, the linear correlation of copper and iron calibration plots reach 99.9%. It is worth noting that the injection of large amounts of organic solvents into the plasma results in a deterioration of the precision of measurements[5], which leads to that sensitivity of direct injection method was only 1/10 of that of another 2 methods because of the formation of carbon
containing ions. What’s worse, oil sample had to be diluted before injection to reduce its viscosity, which further reduced the sensitivity of direct injection method.

In order to avoid the interference of iron and copper in the reagent, the blank test was carried out according to ashing method, acid dissolution method and direct injection method. The blank of copper were 0.4, 0.7 and 0.2 μg/kg, while iron were 9.9, 11.3 and 0 μg/kg respectively. The results indicated that reagents used for inorganization of transformer oil contained few iron contents. LOD of different methods were determined by blank tests and results were shown in Table 2.

\[
\begin{align*}
\text{Table 2} & \quad \text{Comparison of the LOD of different methods(μg/kg)} \\
\text{Isotope/element} & \quad \text{Ashing} & \quad \text{Acid dissolution} & \quad \text{Direct injection} \\
^{63}\text{Cu} & \quad 1.6 & \quad 2.2 & \quad 5.4 \\
^{57}\text{Fe} & \quad 13.3 & \quad 16.2 & \quad 9.8
\end{align*}
\]

Sample A (unused transformer oil) and sample B (running transformer oil) were determined after pretreating by above three methods. In order to obtain accurate results, 6 samples were taken as parallel comparison for each method. Average were obtained by removing outliers and standard deviations of
determination were expressed by SD shown in Table 3. The results showed that pretreatment method had no significant effect on determination of copper contents in both sample A and B, while direct injection method performs best in reproducibility.

In determination of iron contents in sample A, the results obtained by all pretreatment methods were basically consistent. The results of sample B pretreated by ashing and acid dissolution were close and the latter can apply a better reproducibility. Ashing brought a larger bias because of contaminations introduced by environment and incomplete acidic dissolution in pretreatment process. However, direct injection method has low reliability in determination of iron contents in running transformer oil, which might be explained by the fact that iron elements mainly existed in unused oil as soluble compounds, while mostly in so heavy particle state that cannot enter the atomizer of ICP-MS in running contrast[6].

| Table 3 (a) Results of copper Contents in sample A |
|-----------------------------------------------|
|                  µg/kg | Average | SD |
|---------------------|---------|----|
| 1 2 3 4 5 6         |         |    |
| Ashing              | 15.4    | 22.6 |
|                     | 25.2    | 20.2 |
|                     | 24.4    | 11.5 |
|                     | 22.6    | 2.22 |
| Acid dissolution    | 23.4    | 22.8 |
|                     | 23.1    | 24.0 |
|                     | 16.8    | 21.9 |
|                     | 23.0    | 0.78 |
| Direct injection    | 23.6    | 23.2 |
|                     | 23.5    | 23.1 |
|                     | 22.4    | 22.7 |
|                     | 23.1    | 0.46 |

| Table 3(b) Results of copper Contents in sample B |
|-----------------------------------------------|
|                  µg/kg | Average (µg/kg) | SD |
|---------------------|-----------------|----|
| 1 2 3 4 5 6         |                 |    |
| Ashing              | 525.4           | 560.3 |
|                     | 543.4           | 564.2 |
|                     | 538.1           | 240.1 |
|                     | 546.3           | 16.03 |
| Acid dissolution    | 536.4           | 543.3 |
|                     | 547.2           | 555.8 |
|                     | 467.4           | 560.3 |
|                     | 548.6           | 9.59 |
| Direct injection    | 560.6           | 569.7 |
|                     | 559.7           | 553.5 |
|                     | 572.2           | 562.5 |
|                     | 563.0           | 6.88 |

| Table 3 (c) Results of iron Contents in sample A |
|-----------------------------------------------|
|                  µg/kg | Average (µg/kg) | SD |
|---------------------|-----------------|----|
| 1 2 3 4 5 6         |                 |    |
| Ashing              | 67.0            | 65.2 |
|                     | 24.4            | 62.7 |
|                     | 32.6            | 106.3 |
|                     | 65.0            | 2.16 |
| Acid dissolution    | 62.1            | 68.3 |
|                     | 69.3            | 48.2 |
|                     | 60.1            | 66.3 |
|                     | 66.0            | 2.96 |
| Direct injection    | 65.4            | 64.3 |
|                     | 65.7            | 66.4 |
|                     | 65.3            | 63.8 |
|                     | 65.2            | 0.95 |

| Table 3 (d) Results of iron Contents in sample B |
|-----------------------------------------------|
|                  µg/kg | Average (µg/kg) | SD |
|---------------------|-----------------|----|
| 1 2 3 4 5 6         |                 |    |
| Ashing              | 262.1           | 490.6 |
|                     | 246.3           | 274.4 |
|                     | 53.5            | 82.1 |
|                     | 261.9           | 14.09 |
| Acid dissolution    | 255.6           | 258.8 |
|                     | 250.0           | 165.3 |
|                     | 246.4           | 270.3 |
|                     | 256.2           | 9.23 |
| Direct injection    | 0               | 0.34 |
|                     | 0               | 0   |
|                     | 0.13            | 0.22 |
|                     | 0               | /   |

Time consuming for each pretreatment method had also been compared. Direct injection method was mainly spent on ultrasonic vibration which was almost negligible. In addition, reproducibility of direct injection method was so high that it had a great efficiency in determination of unused transformer oil. Acid dissolution method can not batch process and took 1 hour to pretreat a single sample, so its efficiency was limited by reaction equipment. Ashing method that belonged to wet digestion took about 6 hours at all and can process 12 samples at a time. However, the operation process was so easy to introduce impurities that led to incredible results. In order to ensure the accuracy of determination, we had to increase the number of parallel samples, which took longer time and reduced efficiency.
4. Conclusions
ICP-MS is a common technique in determining copper and iron in transformer oil. The accuracy and efficiency of three pretreatment methods had been compared in this paper. The direct injection method is so simple and time-consuming that can realize accurate determination of copper in oil, while it is not suitable for determination of iron in used transformer oil. Acid dissolution method has good accuracy and reproducibility for the determination of new oil and running oil. The single processing time is short, while the determination of batch samples takes a long time. It is suitable for the determination of copper and iron in transformer oil under the condition of ensuring the high operation level of the laboratory personnel. Ashing method performs worst in reproducibility, which is time-consuming and tedious in operation.

References
[1] Ye Z, Zhu Z, Ma N, et al. Copper particle contamination detection of oil-immersed transformer using laser-induced breakdown spectroscopy[J]. Spectrochimica Acta Part B: Atomic Spectroscopy, 167.
[2] Rodriguez D M, Acevedo Aguilar F J, Wrobel K, et al. Spectrophotometric assay for copper and iron in transformer oil using partial least squares regression (PLS2)[J]. Dielectrics & Electrical Insulation IEEE Transactions on, 2006, 13:1272-1277.
[3] Cheng Y. Determination of Iron, Copper, Lead, Tin, Arsenic, Silver, Chromium, Nickel and Vanadium in Oil by Inductively Coupled Plasma Mass Spectrometry[J]. Chinese Journal of Inorganic Analytical Chemistry, 2011.
[4] E.J. Llorent-Martínez, Ortega-Barrales P, M.L Fernández-de Córdova, A. Domínguez-Vidal, A. Ruiz-Medina. Investigation by ICP-MS of trace element levels in vegetable edible oils produced in Spain[J]. Food Chemistry, 2011, 127(3):1257-1262.
[5] Lienemann C P, Dreyfus S, Pecheyran C, et al. Trace metal analysis in petroleum products: Sample introduction evaluation in ICP-OES and comparison with an ICP-MS approach[J]. Oil & Gas Science and Technology - Revue de l"IFP, 2007, 62(1):69-77.
[6] Soin A V, Maryutina T A, Arbuzova T V, et al. Sample preparation in the determination of metals in oil and petroleum products by ICP MS[J]. Journal of Analytical Chemistry, 2010, 65(6):571-576.