Determination of Sulfur Compounds in Hydrotreated Transformer Base Oil by Potentiometric Titration

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A method was developed to analyze the distribution of sulfur compounds in model sulfur compounds by potentiometric titration, and applied to analyze hydrotreated transformer base oil. Model thioethers were oxidized to corresponding sulfoxides by tetrabutylammonium periodate and sodium metaperiodate, respectively, and the sulfoxides were titrated by perchloric acid titrant in acetic anhydride. The contents of aliphatic thioethers and total thioethers were then determined from that of sulfoxides in solution. The method was applied to determine the organic sulfur compounds in hydrotreated transformer base oil.

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Introduction

In general, transformer oil is a product of petroleum refining and a complex mixture of paraffin, naphthene and aromatic compounds. Small amounts of derivatives of hydrocarbons that include atoms of other elements, such as nitrogen, sulfur, and oxygen, also enter into the composition of transformer oil. The oxidation stability of transformer oil is one of main performances, and it is of great concern by transformer oil manufacturers and consumers. There are many factors that affect the oxidation stability, including oil composition, storage and service. In particular, it is greatly affected by the amounts and composition of the sulfur compounds in oil.

Sulfur compounds can improve the oxidation stability of lubricating oil, and some of them are considered to be natural antioxidants.¹⁻³ Even though some sulfur compounds can improve the oxidation stability of oil, not all sulfur compounds have favorable effects. There are corrosive and non-corrosive sulfur compounds in base oil, for example mercaptans, thioethers, thiophenes and disulfides. The oxidation resistance of sulfur compound is different for different molecular structures.⁴ Since these days transformer base oil is mostly hydrotreated, there are only small amount of mercaptans and disulfides. As a result, it is necessary to clarify the distribution of thioethers and thiophenes to improve the oxidation stability in base oil.

Chemical and instrumental methods were emphasized concerning oxidative approaches for thioether analysis. A microchemical method based on bromine oxidation was described by Belcher and co-workers. Direct titration on small samples (about 50 µg) was accomplished by employing 0.02 mol dm⁻³ KBrO₃. However, some problems with overoxidation were also reported.⁵ The oxidation of thioethers with hypochlorite was reported by Leutch. This method employed a

0.1 mol dm⁻³ sodium hypochlorite solution, but a more dilute hypochlorite solution was found to rapidly deteriorate. Thus, difficulties were encountered when adapting the method to the micro scale.⁶ D'Alonzo reported that organic thioethers were oxidized to the corresponding sulfoxides using aqueous sodium metaperiodate. Simultaneously, the periodate was reduced to iodate, which could be quantitatively precipitated by the addition of silver ion in nitric acid. The precipitate was filtered and dissolved in ammonium hydroxide, and the resulting solution was analyzed for its silver content by atomic-absorption spectrometry.⁷ Puchalsky described a method for the analysis of organic thioethers by titration of their hydrogen peroxide-formed sulfoxides. Thioethers were treated with hydrogen peroxide in acetic acid at room temperature to produce the corresponding sulfoxides. Subsequent potentiometric titration of the formed sulfoxide derivative in acetic anhydride was accomplished using HClO₄. The oxidation conditions were hard to control. If the oxidation time and temperature were not suitable, hydrogen peroxide could oxidize thioethers to sulfones, and the result was not accurate.⁸

The goal of the experiment was to develop a simple method for the determination of organic aliphatic thioethers, total thioethers with high selectivity; it was then applied to analyze hydrotreated transformer base oil obtained from Kelamayi Petro-chemical Corporation (Xinjiang, China); the contents of mercaptans and disulfides were too low to be measured in our previous experiment.

Experimental

The principle of the experiment

Sulfoxides present measurable basicity, and can be titrated in acetic anhydride. Thioethers are oxidized to sulfoxides by periodate, and the concentration of sulfoxides is determined by potentiometric titration. The content of thioethers is obtained from the following equation:

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Table 1 Concentration of each sulfur compound in a sulfur compounds solution

Sulfur compound	Weight/mg	Concentration of S/ $\mu\text{g g}^{-1}$
Butyl thioether	115.7	126.80
Dodecyl thioether	216.3	93.55
Ethyl phenyl thioether	63.7	73.88
Phenyl thioether	144.8	124.63
Dibenzothiophene	144.5	125.74

Apparatus

A Metrohm 796 titrprocessor, fitted with glass and saturated calomel electrodes, was used to plot the titration curves of the sulfoxides.

Reagents

n-Butyl thioether, *n*-dodecyl thioether, ethyl phenyl thioether, phenyl thioether and dibenzothiophene were all purchased from TCI. All sulfur compounds were of the purest grades available. Model sulfur compounds were accurately weighted and dissolved in 200 g of ethylbenzene. Table 1 gives the concentration of sulfur of each sulfur compound in solution. The solution was used immediately after preparation. Tetrabutylammonium periodate (certified ACS) was purchased from Aldrich. Sodium metaperiodate was purchased from Shanghai Chemical Reagent Corporation. An aqueous solution containing 25 g dm⁻³ sodium metaperiodate was prepared by dissolving 2 g of sodium metaperiodate in 80 cm³ of distilled deionized water. Although the reagent was stable, it was stored in the dark if it was to be used over an extended period of time.

Perchloric acid titrant: A 0.1 mol dm⁻³ solution was prepared by diluting 9 cm³ of 70% perchloric acid in 1 dm³ of purified dioxane. The solution was allowed to stand 24 h before use. The titrant was standardized potentiometrically against a KI solution.

Calibration of perchloric acid titrant: A KI solution was prepared by dissolving 17 g of KI in 1 dm³ distilled water. The concentration of KI was used as the calibration solution. The concentration of perchloric acid titrant was calibrated as 0.09792 mol dm⁻³ by the calibration solution.

Procedure

A 4 g solution containing the model sulfur compounds was oxidized by 150 mg of tetrabutylammonium periodate in a 250 cm³ ground round-bottom flask, and provided a 5-times molar excess of periodate to sulfur compounds; 10 cm³ of methanol and 50 cm³ of benzene were used as the solvent. The mixture was stirred and heated under reflux for 3 h. The solvent was evaporated under vacuum, and dioxane was added to dissolve the sulfoxides. The bottom flask was washed several times with 10 cm³ of dioxane. The flushing fluid was merged and the solution was accurately weighed. An aliquot of the solution was weighed accurately and dissolved in acetic anhydride. The solution containing sulfoxides was titrated while being stirred. Titration was performed at room temperature (25°C). The electrode was equilibrated in the sample solution before titration. The potential readings were plotted as a function of the added reagent volume. The inflection point of the potentiometric curve, indicating the equivalence point, was located from the point where $\Delta^2 E / \Delta V^2$ became zero. The content of aliphatic thioethers could be calculated from the

Fig. 1 FPD chromatography of the product oxidized by tetrabutylammonium periodate or sodium metaperiodate. A, model sulfur compounds; B, the product oxidized by tetrabutylammonium periodate; C, the product oxidized by sodium metaperiodate. Conditions: 25 m $\times$ 0.53 mm glass capillary, temperature held at 80°C for 1 min and programmed from 80°C to 300°C at 10°C min⁻¹ and then held for 10 min (Shimadzu GC-2010).

Fig. 2 $[M+1]^+$ mass spectra of the product oxidized by tetrabutylammonium periodate or sodium metaperiodate. A, the product oxidized by tetrabutylammonium periodate; B, the product oxidized by sodium metaperiodate. Conditions: vaporizer temperature set at 450°C, capillary temperature at 100°C and corona at 30 eV (ZMD micromass spectrometer, Waters).

amount of perchloric acid titrant used at the inflection point.

The procedure for determining the content of total thioethers was almost the same as that mentioned above. The differences were as follows: a 4 g solution containing the model sulfur compounds was oxidized by 6 cm³ of aqueous sodium metaperiodate, and it provided a 10-times molar excess of periodate to sulfur compounds; 30 cm³ of acetone was used as the solvent. The reaction lasted for 30 h under reflux. The content of the total thioethers was calculated from the amount of titrant used, and the content of aromatic thioethers was obtained from the difference between the content of total thioethers and the content of aliphatic thioethers.

The sulfur compounds in hydrotreated base oil were determined by the same method. Two 20-g samples of base oils were oxidized with tetrabutylammonium periodate and sodium metaperiodate, respectively. The oxidation conditions were the same as those mentioned above. The amounts of two oxidants were 0.23 g and 9 cm³. The contents of aliphatic and aromatic thioethers were calculated from the amounts of perchloric acid titrant.

Results and Discussion

Conditions of the oxidation reaction

Staniello and Manzocchi reported that sulfoxides were

Table 2 Influence of a soluble oxidant on the titration

Sort	Amount/g				Theoretical concentration of sulfoxide group/ $\mu\text{g g}^{-1}$	Amount/ cm^3	Concentration of sulfoxide group found/ $\mu\text{g g}^{-1}$
	Dimethyl sulfoxide	Dioxane	Tetrabutylammonium periodate	Solution		Titration used	
I	0.0246	103	None	52.6103	146.89	1.627	145.55
II	0.0375	102	0.052	49.7130	226.08	2.436	230.63

Table 3 Determination of sulfur compounds in model sulfur compounds solution by potentiometric titration

Analyte	Theoretical concentration of S/ $\mu\text{g g}^{-1}$	The amount of perchloric acid titrant used/ cm^3	Concentration of S found/ $\mu\text{g g}^{-1}$
Aliphatic thioethers	220.35	0.289	226.96
Aromatic thioethers	198.51		187.71
Total thioethers	418.86	0.528	414.67
Thiophenes	125.74		129.93

Fig. 3 Titration of dimethyl sulfoxide in solution.

selectively prepared by the oxidation of thioethers with tetrabutylammonium periodate in chloroform under heating.⁹ Xu reported that tetrahydrothiophene was oxidized to the corresponding sulfoxide by tetrabutylammonium periodate under reflux, but chain aliphatic thioethers were not studied.¹⁰ It was proved that the tetrabutylammonium periodate was a good oxidant, and only aliphatic thioethers were oxidized to the corresponding sulfoxides, not to sulfones, in our experiments. The experimental results are shown in Figs. 1 and 2. In Fig. 1, the compounds of peaks 1 to 5 are butyl thioether, ethyl phenyl thioether, phenyl thioether, dibenzothiophene and dodecyl thioether, respectively.

The results oxidized by sodium metaperiodate are shown in Figs. 1 and 2. Sodium metaperiodate was found to be a good oxidant to oxidize all thioethers completely to sulfoxides without any further oxidation to sulfones. D'Alonzo reported that quantitative oxidation was accomplished under mild conditions (0 – 25°C, 15 h).⁷ It was different from what D'Alonzo reported, that the reaction in our experiments called for a reaction time of 30 h under reflux. The concentrations of sodium metaperiodate and thioethers are not critical in this procedure, because the quantitative oxidation of thioethers to sulfoxides can be accomplished over a large range of concentrations without producing of higher oxidized species, such as sulfones. Many other functional groups, such as benzyl, phenyl, and carboxyl, do not interfere,⁷ and dibenzothiophene can not be oxidized by sodium metaperiodate under the experiment conditions, so the method is selective.

Influence of a soluble oxidant on titration

In the experiments, solutions of two types, *i.e.*, (I) dimethyl sulfoxide in dioxane and, (II) dimethyl sulfoxide and tetrabutylammonium periodate in dioxane, were titrated by perchloric acid titrant in acetic anhydride in order to study the influence of a soluble oxidant on the inflection point. The amounts of dimethyl sulfoxide, tetrabutylammonium periodate and dioxane are given in Table 2. The typical potentiometric curve of dimethyl sulfoxide is shown in Fig. 3. From the result of Table 2, tetrabutylammonium periodate has little effect on the titration of dimethyl sulfoxide. Because sodium

metaperiodate can hardly dissolve in dioxane, it does not have any influence on the result of titration. Because thioethers and sulfones in solution exhibit no measurable basicity in acetic anhydride when they are titrated with perchloric acid,¹¹ the thioethers and oxidants, which do not react, have no influence on the results of titration, and the oxidation products can be titrated directly without further treating.

Determination of the concentrations of sulfur compounds in model sulfur compounds and base oil

The oxidation products of model sulfur compounds were titrated respectively. The amounts of perchloric acid titrant used and the concentrations of aliphatic thioethers and total thioethers are given in Table 3. The concentration of thioethers was calculated from the concentration of the sulfoxide group, and the concentration of aromatic thioethers was obtained from the difference between the concentration of total thioethers and that of aliphatic thioethers. The concentration of thiophenes is obtained from the difference between the concentration of the total sulfur compounds (concentration prepared) and that of the total thioethers. Since the recovery of aliphatic thioethers was 103%, and the recovery of aromatic thioethers was 94.56%, the method for determining the aliphatic and aromatic thioethers is feasible.

In base oil, the content of nitrogen compounds was $1 \mu\text{g cm}^{-3}$, and it could not have any influence on the potentiometric titration. The concentration of the total sulfur compounds (including thiophenes) was determined by the ASTM D 3120 method. The method was used to determine the total content of sulfur compounds in liquid petroleum hydrocarbons by oxidative microcoulometry, and can be described as follows. A liquid sample was injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80% oxygen and 20% nitrogen. Oxidative pyrolysis converted the sulfur to sulfur dioxide, which then flowed into a titration cell where it reacted with triiodide ion present in the electrolyte. The triiodide thus consumed was coulometrically replaced and the total current required to replace it was a measure of the sulfur present in the injected sample. The concentrations of

Table 4 Determination of sulfur compounds by potentiometric titration and ICP-AES in base oil

Analyte	The amount of perchloric acid titrant used/cm ³	Concentration of S found by potentiometric titration/ $\mu\text{g g}^{-1}$	Concentration of S found by ICP-AES/ $\mu\text{g g}^{-1}$
Aliphatic thioethers	0.073	11.4	12.3
Total thioethers	0.187	29.3	30.4
Thiophenes		80.7	79.6
Sulfur compounds		110	110

aliphatic and total thioethers were determined by the method for analyzing the model sulfur compounds and the concentrations of aromatic thioethers and thiophenes were calculated. The results are given in Table 4. The content of thioethers was low in base oil, which accords with the oxidation method and ICP-AES in our previous study.

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