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Physical and chemical methods of organic impurities control in the feed water of waste heat boilers of thermal power plants

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Abstract. For the quantitative control of the organic impurities content in deeply purified waters, a simple, effective and inexpensive method with the carbon tetrachloride extraction was developed for waste heat boilers feeding. The presented methodology served to study the organic substances content in the nutrient water of the Kazan CHP-1 and Kazan CHP-3 waste heat boilers. According to the results of various physical and chemical methods, the samples extracted from feedwaters of waste-heat boilers have been examined for their qualitative composition. The discovered organic substances belonged predominantly to the class of humic substances, which, due to their physicochemical properties, can penetrate into all types of deeply treated water. The proposed method for complex determination of organic impurities by extraction in the feedwaters of a waste-heat boiler may be used as an alternative to the total organic carbon analysis.

1. Introduction

In connection with the widespread commissioning of combined-cycle plants with waste-heat boilers in the last decade, close attention has been paid to the noticeable effect of organic impurities on the quality of steam in the steam-water tract of the TPP. The organic substances content in natural water is many times higher than the content of inorganic ones. They are very diverse in their composition and properties. Under the action of high temperatures, organic impurities can be modified and transformed into substances potentially dangerous to thermal equipment. The literature describes emergencies that led to serious damages to heat and power equipment, caused by the proven presence of large amounts of organic substances in the feed tract [1, 2]. With the advent of new technologies, as well as with the rationing of the added water quality for total organic carbon, the water treatment at all levels is constantly being improved [3-6].

It should be noted that control over organic impurities concentration in the liquid and vapor phases poses significant difficulties [7]. Moreover, earlier it was believed that the impact of organic impurities on the system of steam-water path is minimal or insignificant. In this regard, the methods of their analysis were almost set aside. In the standard system of chemical control at power plants, organic impurities are controlled only at the water pretreatment stage, i.e. at the coagulation and filtration stage. Like decades ago, the color of water (organic humus acids are colored), permanganate, rarely bichromatic oxidation or chemical oxygen consumption are determined.

For the deeply purified water analysis for organic component, the total organic carbon analyzers are used. They proved to be the "gold standard" of evaluation. However, in domestic power plants, the widespread use of these devices is limited by their high cost. The total organic carbon indicator is considered an integral method and depends on the method used to oxidize the sample. The principle of some analyzers operation is based on the dry burning method, which is difficult to perform, but fully



reflects the organic impurities in the water volume. In order to reduce the cost of continuous control equipment, a number of analyzers use an oxidation method based on sample irradiating with hard ultraviolet light in the presence of persulfate on a titanium oxide catalyst. However such a method does not ensure complete oxidation for a number of substances. So, humic acids are oxidized by about 30-50%, fulvic acids – by 50-60%, and dichloroethane remains almost unoxidized. At the same time, benzoic rings are perfectly destroyed. As a result, the total organic carbon, determined in this way, erroneously shows greatly underestimated values [2]. One of the most successful options is the analyzer, based on the high-temperature catalytic oxidation of carbon compounds in the water sample. These analyzers provide separate determination of total carbon and total inorganic carbon.

In addition, less expensive methods based on the results of conductometric and optical measurements are presented in works performed in the laboratory and at operating TPP for the organic impurities content monitoring. Thus, a number of authors propose to evaluate the organic substances content by the value of specific conductivity (χ) in various types of deeply purified water [8,9], or by the value of pH (pH) [10], as well as by the value of light transmission in the UV untreated water [7]. It should be noted that impurities in water have a multifactorial effect on χ and pH, so this method of evaluation is not informative.

Thus, there is a clear need to develop a simple, accurate and inexpensive method for the quantitative analysis of organic impurities in deeply treated TPP waters.

2. Materials and methods

For quantitative and qualitative analysis of organic impurities, samples were taken from different parts of the feedwater preparation cycle for the waste-heat boiler and from the steam-water tract of the Kazan Thermal Power Plant-3 and Kazan Thermal Power Plant-2: the main turbine condensate, the feed water of the waste-heat boiler, the purge water of the waste-heat boiler, chemically desalinated water, evaporative distillate, and purge water of clarifiers. Taking into account the fact that the expected concentration of organic substances in the feed waters is no more than 1 mg / l, the necessary amount for a detailed analysis of each type of water was taken in a volume of at least 10 liters.

Organic compounds from water samples were extracted with carbon tetrachloride (CCl_4) in a separatory funnel. For these purposes, 100 ml of carbon tetrachloride was taken for 1 liter of desalted water and mixed vigorously for 5 minutes. Then a portion of the separated extract was taken and the procedure was repeated until the total volume of the test water was about 10 liters. Next, portions of the obtained extracts were combined and the samples were dried at 25 ° C. The dry residue was weighed on an analytical balance; the organic substances concentration in the studied types of water and the total organic carbon content were calculated in $\mu\text{g} / \text{l}$.

To qualitatively confirm the organic nature of the obtained extracts, as well as to control the proposed method effectiveness and accuracy, samples of extracted organic substances were subjected to infrared spectroscopy, high performance liquid chromatography (HPLC), mass spectroscopy, and nuclear magnetic resonance.

3. Results Introduction

The isolated organic substances were crystalline or resinous non-volatile substances from white-yellow to bright orange. In terms of total organic carbon, the organic substances concentration met the requirement of technical operation of thermal stations and electrical networks of the Russian Federation [11] and the standard of organization STO VTI - 2009 [12] for all investigated water samples, except feedwater of the waste-heat boiler, showing a 2-3 times excess. The measurement accuracy was $\pm 10\%$.

By the nature of the impurities contained in the samples under study, all the chemical analysis methods have established the presence of predominantly humic substances with some other organic molecules. These results indicate a good solubility of humic substances, their slipping through ion-exchange filters and transfer with some steam fractions due to thermal stability.

According to the results of HPLC studies, peaks with a release time of 3–7 minutes and 23–25 minutes characteristic of humic acids can be traced in all spectra of the studied samples [13]. Compounds with an exit time of 3–7 minutes are hydrophilic, since they elute from the column with water and have a low retention time. Compounds with a release time of 25 minutes are hydrophobic, and humic acids they are of aromatic nature and are eluted from the column with acetonitrile. On the ratio of the area under the peaks at different optical densities it may be concluded that the selected humic substances have a small level of specific aromaticity of the total fractions. The content of aromatic fractions indicates the degree of humic substances humification. A large number of peaks in the studied samples' chromatograms (more than 20) characterize a large number of aliphatic and aromatic fragments, including $-\text{COOH}$, $-\text{OH}$, $-\text{COO}-$, $-\text{C} = \text{O}$, aromatic rings and aliphatic substituents (figure 1).

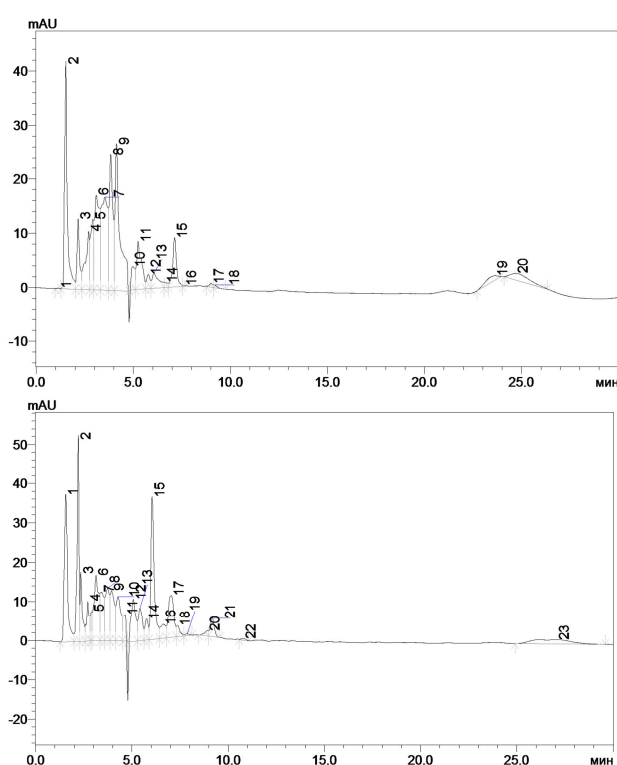


Figure 1. Chromatogram of the purge water sample extract of the waste-heat boiler (a), chemically desalinated water (b) at 220 nm.

As a result of the mass spectrometric analysis of the main turbine condensate and the waste heat boiler feedwater, satisfactory mass spectra were obtained only in the case of the main turbine condensate. Due to the specific nature of the mass spectrometry analysis, it can detect not very large organic molecules. Humic substances, for example, due to the large molecular weight, are difficult to identify with this method. It was assumed that the main group of organic substances in all types of investigated waters is humic substances. In addition to them, the main turbine condensate sample contains presumably impurities from the suction cups of cooling water, detected by the gas-mass spectrometry method. In the waste heat boiler feedwater, these substances are already in a highly diluted state and no significant signals could be obtained.

To determine the presence of organic components, NMR ^1H spectra were recorded for all samples. The analyzed samples according to the NMR ^1H results (figure 2) are solutions in CDCl_3 containing alcohol groups, n-alkanes C12-C18, PEG-400 and silicone (silanes) in different ratios. There is a slight

peak in all spectra in the region of 5.3 ppm, which may correspond to unsaturated groups $RCH=C<$. Due to the fact that in the studied solutions organic substances are presumably humic compounds, more precisely, salts of humic and fulvic acids with metals (Na, Ca, etc.), the COOH group is absent or poorly expressed in their PMR spectra. Since the x-axis on the graph ends at a value of 8 ppm it is not possible to assess the chemical shifts presence in the region of 10–12 ppm, which corresponds to carboxylic acids [14].

In addition, PEG-400 – highly soluble and heat resistant anticorrosive additive – was found in all types of water.

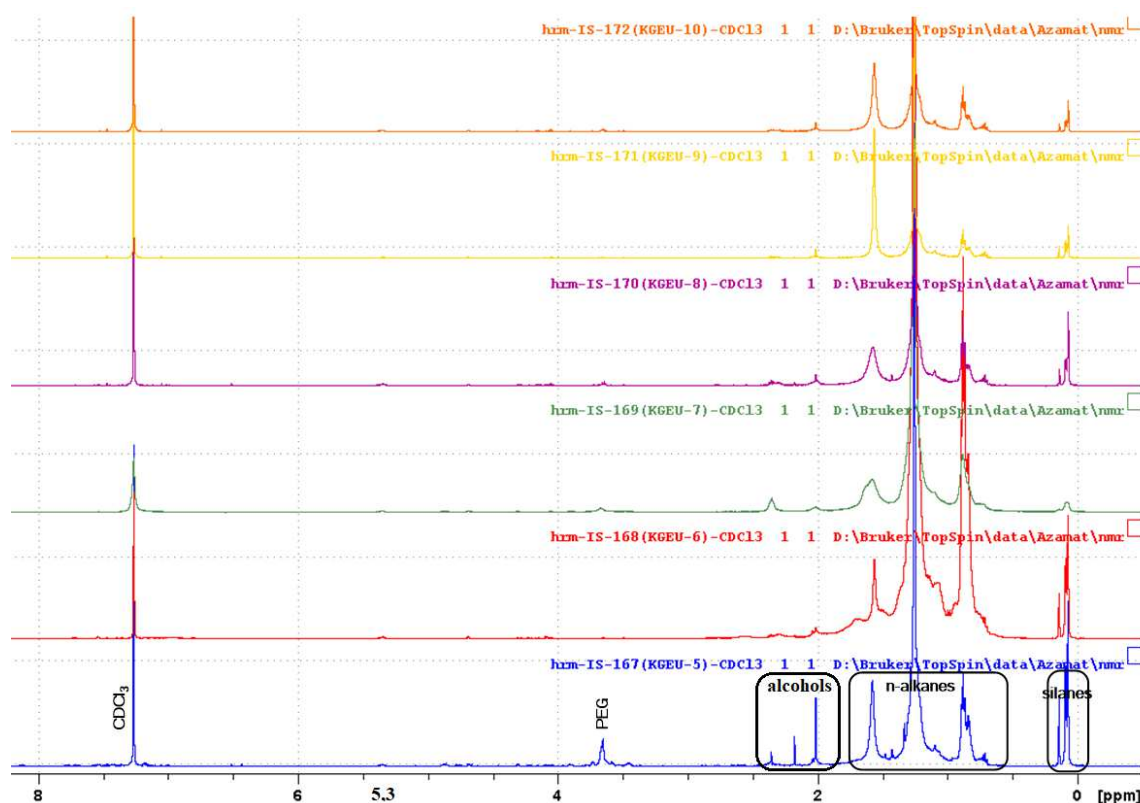


Figure 2. NMR 1H spectra for: the main turbine condensate, the waste-heat boiler feedwater, the waste heat boiler purge water, the chemically desalinated water, purge water of continuous cycle clarifiers, purge water of periodic cycle clarifiers (from top to bottom) in $CDCl_3$ solution, 500MHz.

To eliminate the possibility for the impurities contained in the solvent used for extraction (CCl_4) and that for the NMR analysis ($CDCl_3$) to be transferred to the studied samples, the NMR spectra of their mutual solution were additionally recorded. As a result of the NMR data analysis, including two-dimensional correlation spectra, it has been found that, despite the observed impurity signals in the NMR 1H spectrum (which is highly sensitive), any significant impurities according to ^{13}C NMR and 2D correlation spectra in the CCl_4 sample in $CDCl_3$ were noted.

Figure 3 shows the correlation results for the proposed method for organic substance extraction from water and the total organic carbon analyzer. The correlation is more than 99%.

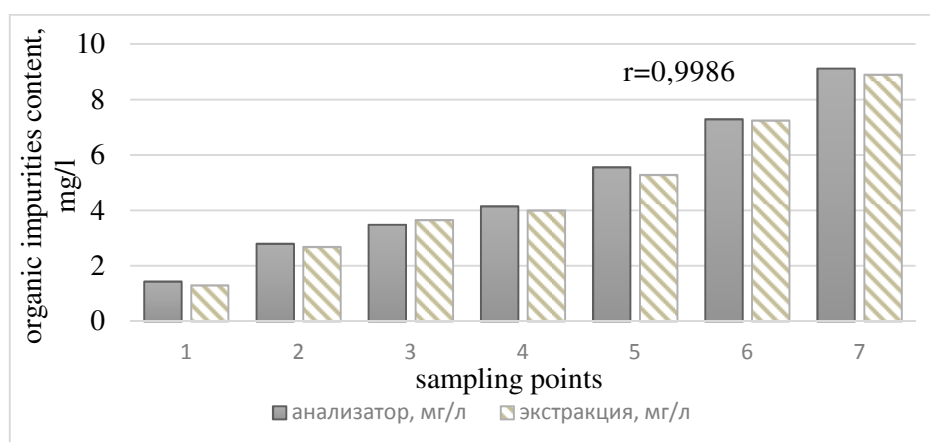


Figure 3. Comparison of the results of determining the TOC on the TOC analyzer and the extraction method.

Conclusion

1. The presented method for analyzing the organic impurities in deeply purified waters is accurate, simple in technical realization and independent of used materials, which together allows using it as an alternative to the total organic carbon analyzer.
2. Humic substances have been identified as the main organic component, determined by various methods of physical and chemical analysis. These are easily water soluble fractions with low specific aromaticity. Due to their physical and chemical properties, humus substances freely pass through the pretreatment stage and penetrate into all types of deeply treated water.

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