METHODS OF ASSESSING FUEL AND OIL QUALITY

STUDY OF THE INFRARED ABSORPTION SPECTRA
OF VARIOUS ADDITIVE ASHES

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Oils with additives are required for operation of modern engines.

As a rule, most of the additives in use substantially improve the quality of the base oils, but they form what are known as ash deposits during operation of the machines and mechanisms. These deposits sometimes give rise to various complications in engine operation.

The nature of the ash deposits depends primarily on the composition of the ash and its properties.

The emission-analysis method now being used extensively and successfully gives us information only on the concentrations of metals and phosphorus. It sheds no light on the chemical composition of the ash.

We used infrared spectroscopy to study ash chemical composition.

The literature offers no studies devoted directly to the infrared spectra of petroleum-product ashes. References [1-4] give infrared spectra for pure salts and various minerals. We ourselves acquired spectra for certain metal salts and oxides. Figure 1 shows the IR absorption spectra of barium, zinc, and magnesium sulfates and zinc, magnesium, and calcium oxides in the 1500-500 cm\(^{-1}\) band.

The analytical frequencies of the salts assumed to be present in the ash are as follows:

For sulfates  \( \ldots 580-640, 1030-1180\ \text{cm}^{-1} \)
For carbonates  \( \ldots 870, 1450\ \text{cm}^{-1} \)
For oxides  \( \ldots 650-750, 1400-1500\ \text{cm}^{-1} \)
For phosphates  \( \ldots 560, 580, 1000\ \text{cm}^{-1} \)

It should be noted that the positions of the band maxima vary appreciably, depending on the nature of the metal. Thus, bands at 610, 635, 1080, 1120, 1180 cm\(^{-1}\) are characteristic for barium sulfate and bands at 667, 1010, and 1130 cm\(^{-1}\) for calcium sulfate.

The IR spectra of the additive and additive-oil ashes were obtained on a UR-10 infrared spectrometer. Ash specimens were mixed with potassium bromide in 1:100 proportions for 5-10 min in a vibrator and then tableted under a pressure of 200 atm.

TABLE 1. Metal Contents in Ash

<table>
<thead>
<tr>
<th>Ash specimen</th>
<th>Ca</th>
<th>Mg</th>
<th>P</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>31</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>18</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

TABLE 2. Metal Contents in Ash

<table>
<thead>
<tr>
<th>Ash specimen</th>
<th>Ba</th>
<th>Zn</th>
<th>P</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.0</td>
<td>5.0</td>
<td>4.6</td>
<td>0.03</td>
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<tr>
<td>2</td>
<td>74.5</td>
<td>5.0</td>
<td>3.7</td>
<td>0.04</td>
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<tr>
<td>3</td>
<td>73.0</td>
<td>4.5</td>
<td>3.4</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>77.0</td>
<td>4.5</td>
<td>3.5</td>
<td>0.04</td>
</tr>
</tbody>
</table>

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Fig. 1. IR spectra of sulfates and oxides of various metals: a) ZnO; b) CaO; c) MgO; d) ZnSO₄; e) MgSO₄; f) BaSO₄.

Fig. 2. IR spectra of ash obtained under various conditions from additive mixes: a) 800°C without ammonium nitrate treatment; b) 550°C with ammonium nitrate treatment; c) 1000°C with ammonium nitrate treatment; d, e, f, g) IR spectra of ashes from various additives and additive mixes.

The effects of temperature and calcination conditions on ash composition were determined in the infra-red-spectrometry study of ash chemical composition. For this purpose, the additive was calcined under various conditions, and the IR spectra of the resulting ashes were examined. As an example, we present data from the analysis of three ash specimens. The first specimen was produced by calcination at 800°C (Fig. 2a), the second by calcination at 550°C and oxidation with ammonium nitrate (Fig. 2b); the third specimen was prepared in the same way as the second, but with subsequent roasting at 1000°C (Fig. 2c).

On examining these spectra (Fig. 2), we see that despite the equal ash concentrations in the tablets, the bands show differing intensities in the spectra. All of the specimen IR spectra show distinct sulfate absorption bands at 580, 610, and 1030-1180 cm⁻¹. The sulfate absorption is more intense for the ash roasted at 1000°C. The ash prepared at 800°C (Fig. 2a) contains carbonates (870 and 1500 cm⁻¹) and oxides (470, 690 cm⁻¹) of calcium and magnesium. The ash prepared at 500°C (Fig. 2b) contains for the most part calcium and magnesium carbonates. After this ash was roasted at 1000°C (Fig. 2c), the absorption bands characteristic for the carbonates disappeared from the IR spectrum, indicating that the carbonates had been decomposed. The intensity of the 470- and 690-cm⁻¹ bands increased owing to the formation of magnesium and calcium oxides in the ash. The metal contents of the ash, according to emission analysis (Table 1), stand in agreement with the IR absorption spectra.

Thus, the ash of specimen 1 consists of metal sulfates, carbonates, and oxides, and this explains why the calcium and magnesium contents are higher than in specimen 2, which does not contain metal oxides.

Obviously, the composition of the additive ash and, accordingly, the nature of the ash spectra will depend on the calcination technique. Therefore, in order to secure comparable results from investigation of the additive ashes, all additives and additive mixes were thenceforward calcined under identical conditions at 550°C in the presence of ammonium nitrate.

There are substantial differences between the ash IR spectra of the various additives. Figure 2d, e, f, and g, shows IR spectra of ashes from four additives. We see that the specimens studied have characteristic absorption bands in the 580-680, 1000-1200, and 1400-1560 cm⁻¹ regions, but that the shapes, intensities, and positions of the bands are different for each specimen.

Interesting results were obtained from analysis of the ash spectra of additive mixes that differed in chemical structure but contained sulfur and the same metals in the same concentrations, and also showed identical ash contents and alkalinities. Figure 2a and b show the IR spectra of ashes from two additive mixes of closely similar composition. The IR spectra of the specimens are clearly identical. It was found from emission analysis that the contents of barium, zinc, and phosphorus were the same (Table 2, specimens 1 and 2). Sulfates, sulfides, and total sulfur were determined chemically, and their contents were also found to be identical in the two specimens.