METHODS OF ASSESSING FUEL AND OIL QUALITY

FACTORS INFLUENCING THE PRECISION OF DETERMINATION
OF ADDITIVE CONCENTRATION IN AVIATION OILS
USING THIN-LAYER CHROMATOGRAPHY

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For a successful solution of the problem of increasing the efficiency of utilization of aviation oils, evaluation of the oil service properties is of primary importance. In this connection, ever-increasing attention in our country and abroad is being allotted to the development of accelerated methods for rating the quality of aviation oils [1]. Feasibility in principle was demonstrated in [2] for the determination of one of the most important parameters—the exhaustion of antioxidant additives in mineral oils—by thin-layer chromatography. As oils are made up of various classes of organic compounds, it becomes necessary to study the influence of various factors on the determination of additive content; these factors may depend on the oil base stock, the presence of several additives, and on the reagents and equipment used in the determination.

The present investigation was aimed at determining the influence of adsorbent-layer activity, methods of applying the test samples to the plate, and the mobile phase and developing chamber on the accuracy and reproducibility of results from quantitative estimates of additive contents, and was also aimed at establishing the optimal test conditions.

Activity of Sorbent Layer. In thin-layer chromatography, poor reproducibility of the values of $R_f$ for the spots of substances is observed, owing to the extremely unstable level of activity of the thin layer of adsorbent [3].

In the case of using Silufol brand prepared plates (CzechSSR), by monitoring the level of their activity as determined by the procedure of [4], it was found that the moisture content in the sorbent of the factory-packaged plates is about 10%; when the plates are activated as prescribed by Stahl [5] (110°C, 30 min), the moisture content is about 3%; and when they are humidified by storing for 15 h in a closed constant-temperature chamber with saturated aqueous sodium bromide solution, the moisture content of the plants is about 20% [3].

The effect of varying activity of the sorbent layer on the reproducibility of values of $R_f$ was checked in the following manner. One batch of plates was divided into three series; in the first series, spots of a reference substance were deposited immediately, in the second series after activation, and in the third series after humidification. The reference substance was sudan, and the mobile phase was benzene. All plates were developed under identical conditions in a C chamber, to a distance of 10 cm from the line of sample application.

In the first series of plates, the average value of $R_f$ was 0.36 and the coefficient of variation was ±26%; in the second series the respective values were 0.22 and ±37%, and in the third series 0.42 and ±15%. Similar measurements with other batches of plates gave lower values for the coefficient of variation. The application of the spots and the development of the plates were carried out in a direction perpendicular to the direction of application of the absorbent layer, since the reproducibility of $R_f$ was much poorer when the directions of development and sorbent-layer application were the same. All subsequent studies were performed with humidified plates.

Application of Substance to Plate. In testing various methods of applying the samples the following were used: a microsyringe with a micrometer screw and a flexible plunger made of fluoroplastic; a microsyringe with a needle/cylinder with a capacity of 1 µl; and a specially made capillary [6].

Several series of experiments (about 30) were performed with MK-8 oil; spots were applied from each of the devices just listed. When using the syringe with the fluoroplastic plunger, the average spot diameter was...
Mobile Phase. Although some work has been reported \([3-5]\) on the problem of selecting the optimal mobile phase for developing chromatographic plates, the theoretical aspects of this question are not yet worked out adequately. The adsorbent being used—silica gel—is classed among the adsorbents with local positive charge (hydrogen of the silanol hydroxyl). In examining a system consisting of adsorbent and aviation oil with additives, we must observe the interaction of the local positive charge of the active centers of the adsorbent with the \(\sigma\) bonds of the main mass of hydrocarbons of the oil and the \(\pi\) bonds of the hydrocarbons, and to a lesser degree with the local negative charge due to an unshared pair of electrons. On the basis of the theory of short-range intermolecular interactions of Kiselev \([7]\), organic compounds with local negative charges (\(\pi\) electrons, unshared pair of electrons) or compounds with both positive and negative localized charges have strong intermolecular interactions with the active centers of the adsorbent, owing to local changes in electron density of the different molecules. Organic compounds with \(\sigma\) bonds and compounds with local positive charge (active hydrogen) have weak intermolecular bonds as a result of van der Waals forces, when one of the compounds does not have any pronounced local changes in electron density.

In view of these considerations, in resolving the complex problem of segregating additive spots on the plate from the main part of the oil hydrocarbons, work was performed to select solvents of various activities and blends of these solvents for use as the mobile phase for development, choosing the solvents from an elutropic series \([3]\). Even though separation of the additives was achieved in a single development (Figs. 1 and 2), a symmetrical, compact spot shape was obtained only when the additives were applied in carbon tetrachloride; when the additives were applied in oils with various base stocks, the spots were horseshoe shaped and unsatisfactory for further quantitative evaluation. In the subsequent experiments, we used a stepwise development procedure in which the first development of the plate was performed over the entire length, using a solvent with weak eluting activity \(\left(\epsilon^0\right)\), thus separating off the main part of the hydrocarbons with \(\sigma\) bonds; the subsequent development was performed to the standard length of 10 cm with a more active mobile phase (Fig. 3). This procedure gave compact spots on the plate, symmetrical in form, within the limits of required values \(Rf = 0.3-0.8\). Different lube base stocks did not have any effect on the value of \(Rf\) for the additive spots.

Conditions of Plate Development. It was established experimentally that the type of chamber in which the chromatographic plates is developed has a great influence on \(Rf\) of the spots of additive and oil base stock, and also on the shape of the additive spots (Table 1). It can be seen from these data that the optimal results, in terms of separating the oil base stock from the additives and obtaining compact, symmetrical spots, were achieved when the plates were developed first in a C chamber and then in a jar (see Table 1, No. 6).