

Spectrophotometric analysis of hydrocarbons in the soil

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For measurements using liquid extraction of hydrocarbons from the soil, a laboratory model of a broadband spectrophotometric analyzer has been constructed based on SA-2 spectrophotometric analyzer of solutions, developed at the Institute of Atmospheric Optics SB RAS. The hydrocarbon absorption spectrum was recorded in several regions: 3–4 μm region of the fundamental transitions, where hydrocarbon absorption spectra are characterized by large values of the absorption coefficient, and in the 1.8–2.5 μm and 0.8–1.6 μm overtone regions where absorption by different hydrocarbon groups is well separated. The wide spectral region, high sensitivity, and efficiency of the spectrophotometer allowed covering a wide dynamic range of measured concentrations (3–4 orders of magnitude) and providing for sufficient selectivity in the hydrocarbon type content and fraction composition.

Introduction

On the Russian market of domestic produced facilities for measurement of the concentrations of oil products, the IR spectroscopy is represented by either integral-bandpass or differential-filter spectrophotometers (about 10 versions of such devices, including IKN-025, are advertised). These are capable of measuring the concentration of State Standard Samples (SSS) and solutions, close to state standards in the composition and spectral parameters, with high reproducibility and accuracy, and these standard samples are also used for calibration of these devices (sometimes, at only one wavelength; for example, KN-2 is calibrated at the wavelength of 3.42 μm). However, they cannot be used for monitoring of the hydrocarbon type content at ageing of oil spills with the variation of the composition in time and with the need to cover a wide dynamic range of the measured concentrations under natural conditions.

For qualitative and quantitative analysis of oil products, polluting the soil, it is necessary:

- to determine the hydrocarbon type content and the fraction composition of oil products;
- to solve the concentration spectroscopic problem for multicomponent mixtures with the possibility of covering a wide dynamic range of the concentrations to be measured.

In the work, to speed-up the analysis and avoid the errors in identification of the composition of real multicomponent mixtures in a wide spectral region, we applied the up-to-date mathematical processing of data and mathematical statistics in combination with the pattern recognition methods. This allowed us to analyze correctly multidimensional data, that is, to use as large information contained in the analyzed spectrum as possible, thus decreasing noise, improving the repeatability of measurements at multiple analysis, etc. Obtaining spectral characteristics, compilation of data banks, search of informative features in spectra and their derivatives, and construction of functional

dependences for quantification of mixtures were carried out in the automatic mode with the use of the original dialog system for spectral analysis. Due to these features, the analyzer developed is advantageous over analogical domestic and foreign devices.

1. Spectrometric solution analyzer

The quantitative and qualitative analysis of liquids is carried out based on the approach, involving the up-to-date mathematical processing of spectral data in combination with pattern recognition methods.

The proposed solution combines three approaches¹ each being of principle importance:

1. Fast spectral scanning, which requires no mechanical tuning to a certain wavelength, but provides for recording the entire spectral range for one turn of a diffraction grating (0.2–2 s).
2. Computer correction of the recorded spectrum ensuring high accuracy characteristics of the spectrophotometer.

3. Information processing with the use of the software based on original pattern recognition algorithms and methods, which allow the recorded pattern to be used as a spectral image, determining the state of an object, for example, the octane number of gasoline.

The spectrophotometer employs the widely used Czerny–Turner scheme (Fig. 1).

The spectrophotometer, including a light source *O*, a photodetector *P*, a sample feed unit *SF*, a diffraction grating with inertial rotation module *BSS*, a LED indicator of the final position of the diffraction grating *M*, and a control unit *CU*, is supplemented with sensors of the angular position of the diffraction grating *D*, a synchronization unit *SU*, an amplifier *A*, a power supply *PS*, and an interface with analog-to-digital converter *I*. The diffraction grating is rotated by the rotation module at a rate of 0.5–5 Hz. The rotation module has high inertia that provides for high stability of the angular speed for

every following displacement between certain angular positions, from which the extrapolation normalization of the spectral signal detected by the photodetector is being carried out.

determining the correction coefficient and re-scaling single output signals on the frequency scale.

The main performance parameters of the spectrometer are given below.

Spectral region, μm	0.2–3.4
Photometric accuracy	0.001
Reproducibility of wavelength setting, nm	0.1
Time for recording of spectrum, s	0.1–1
Maximum rate of spectral scanning, nm/s	3000
Overall dimensions, mm	400 × 330 × 180
Weight, kg	10
Consumed power, W	< 70

The appearance of the spectrophotometric analyzer is shown in Fig. 2.

The original dialog system for spectral analysis² enables the user to independently reveal the relations between the recorded spectra and the sought liquid (for example, oil product) parameter, to compile data banks, to perform the analytical search of the functional dependence between the set of spectral curves of standard solutions and the parameter to be determined. This significantly speeds up the analysis and decreases the probability of misinterpretation in operating with real multicomponent mixtures.

The approach developed significantly increases the sensitivity of the spectral devices used and makes them suitable for solving various problems: from the measurement of low concentrations of absorbing admixtures in liquids to the determination of the type of analyzed substance and different parameters of multicomponent mixtures.

The smart spectrophotometric liquid analyzer simultaneously determines several parameters of the liquid, for example, for gasoline: the fraction composition, the research and motor octane numbers, density, refractive index, dielectric constant, water content, and others, with the presence of a model data bank for each of these parameters; operates in a logical mode; classifies the liquid; compares the analyzed liquid with the reference (standard) one; determines the content of traces by applying the known standard or specially developed techniques.

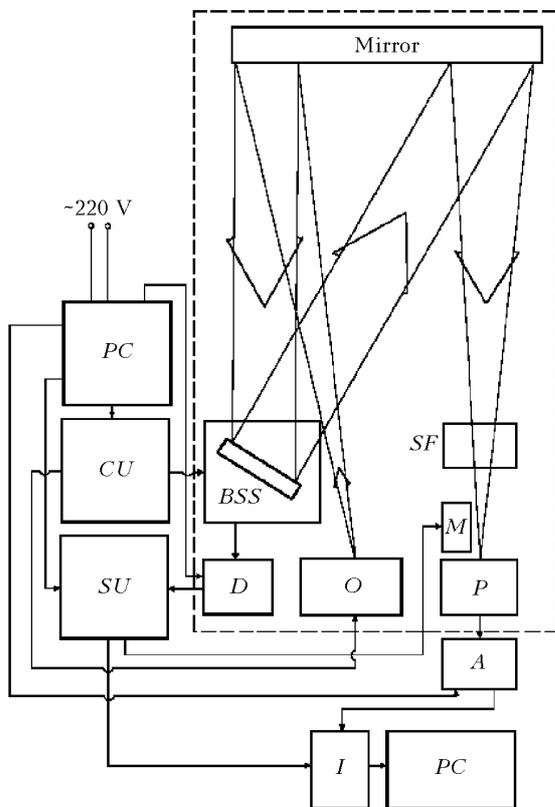


Fig. 1. Functional block-diagram of the device for analysis of liquids.

The sensors of the angular position of the diffraction grating and the synchronization unit enable the influence of grating rotation instability to be minimized with a computer program in recording the spectrum without the use of precision mechanical rotation modules. Once the spectral signal has been obtained, the computer controls the instability of grating rotation and makes the corrections needed by



Fig. 2.

2. General characterization of the hydrocarbon spectra in the near-IR as a part of studying the hydrocarbon type content and fraction composition of oil products

To monitor the soil pollution by oil products during soil reclaiming and to establish the relation to a possible source of pollution and time elapsed from the spill event, the key problem is determination of the hydrocarbon type content and fraction composition of oil products. For solving this complicated problem and find the general regularities in hydrocarbon absorption spectra, we have initially took the spectral range from 0.8 to 1.6 μm . To develop the techniques and algorithms for determination of the hydrocarbon type content and the fraction composition of oil products, we used pure hydrocarbons and their mixtures. The spectra of some pure hydrocarbons are shown in Fig. 3*a*. The survey spectra in Fig. 3*a* are the sets of the bands, corresponding to the second and third overtones of the CH_x -group, vibrations of C–C bonds, and combination frequencies.

Let us present some most general features of the hydrocarbon spectra, using, as an example, CH_x -groups, which determine most properties of the oil products. Figures 3*b* and *c* depict the fragments of the survey spectra shown in Fig. 3*a*, corresponding to the regions of 1.10–1.25 μm for the second overtone and 0.85–0.95 μm for the third overtone of

CH_x -groups. It can be seen from Figs. 3*b* and *c* that the fragments have some similarity, are informative, and can be used for analysis of the mixture composition.

Figure 3*d* shows the spectra of benzol (1), toluol (2), and isooctane (3) in the region of the second overtone of the CH_x -groups. The CH - to CH_3 -group ratios in them are 6/6–0/6, 6/7–1/7, and 0/8–7/8. This corresponds to the increase in the relative intensity of the longest-wave peak (1.19 μm) as we go on to hydrocarbons, containing the larger number of CH_3 -groups. In the spectrum of benzol (1), having only aromatic CH -groups, the corresponding peak lies in the short-wave region (1.135 μm).

Figure 3*e* shows the spectra of normal paraffins: hexane (4), heptane (5), and nonane (6), in the same spectral range. The CH_3 - to CH_2 -groups ratios in them are 2/5–3/5, 2/6–4/6, and 2/9–7/9. This corresponds to an increase in the relative intensity of the longer-wave peak (1.21 μm) as we go on to heavier hydrocarbons, containing the larger number of CH_2 -groups, and to a decrease in the intensity of the peak, corresponding to the CH_3 -group (1.19 μm). It should be noted that the spectra of real oil products, due to the presence of many components in them (paraffins, isoparaffins, aromatics, naphthenes, oliphens, unsaturated hydrocarbons, and others), are characterized by even wider variety of (multidimensional) features.

To confirm this thesis, Fig. 3*f* shows, as an example, the absorption spectra of three gasolines

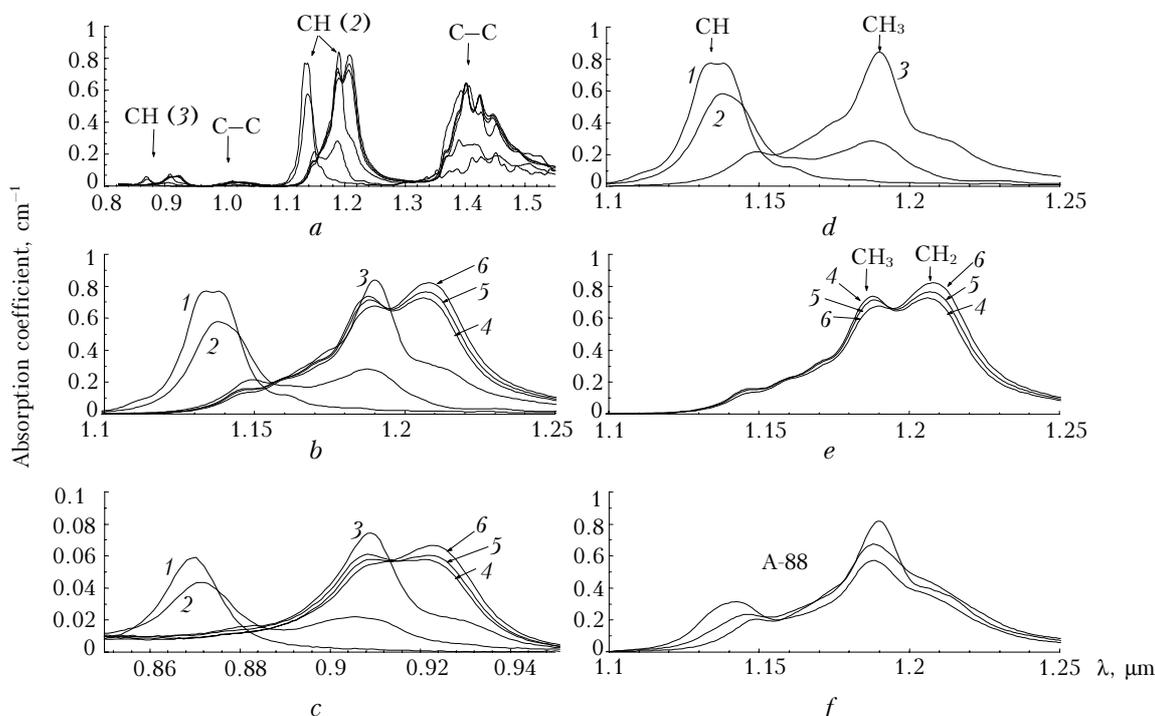


Fig. 3. Examples of IR spectra recorded with the spectrophotometric analyzer: (a) survey spectra; (b, c, d, e) fragments of the spectra of pure hydrocarbons (benzol (1), toluol (2), isooctane (3), hexane (4), heptane (5), nonane (6)); (f) spectra of A-88 gasoline produced by different plants.

from different refineries, produced by different methods, but characterized by the same research octane number equal to 88.

Such differences in the spectra of real multicomponent mixtures prevent unambiguous determination of the oil product parameters by use of the ordinary regression analysis methods. Therefore, the operations with the initial spectral curves aimed at extracting maximum information from them should be based on the combination of methods of serious logical analysis, including cybernetics and pattern recognition methods.

3. Estimated range of measured concentrations

To estimate the range of measured concentrations and to study the sensitivity of the solution analyzer, we used the spectral range of 1.7–3.4 μm . The calibrating solutions with different concentrations of hydrocarbons were prepared through extraction of

provides for a wide range (10^5) of variation of oil product concentration in soil.

Conclusions

We have analyzed the recorded spectra of calibrating mixtures and established the relations between their IR spectra and known quantitative characteristics of the oil products. The fast spectroscopic method, described above, provides for good results in reconstructing the parameters of oil products from their IR spectra, as well as establishes the functional dependences between the set of spectral curves of reference solutions and the value of the parameter to be determined. This shows good promises for the further development of this method for solution of a wide range of research and applied problems, including the monitoring of soil pollution by oil products during the soil reclaiming and the establishment of the relation to a possible source of pollution and time elapsed from the spill event.

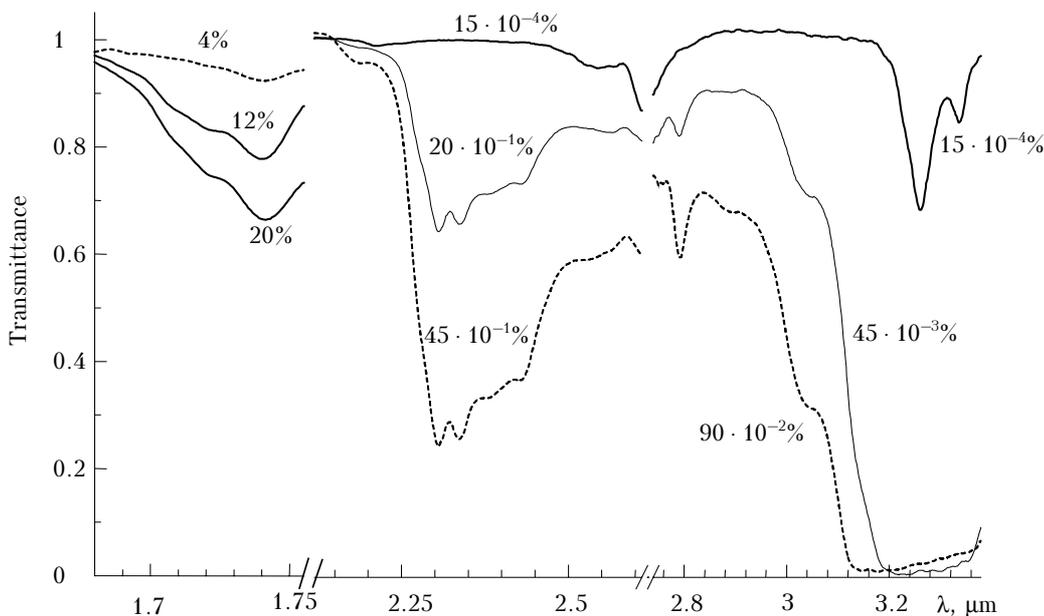


Fig. 4.

oil and black oil from peat and soil. The spectra were recorded in the entire spectral range selected. Figure 4 shows the fragments of several spectra of test solutions.

The wavelength in μm is plotted as abscissa, and the transmittance of the calibrating solutions in a 1-cm thick optical cell is plotted as the ordinate. Each spectrum corresponds to a certain mass concentration of oil products in peat and soil.

It can be seen from Fig. 4 that the analyzer is capable of detecting the oil product concentrations at the level of $10^{-4}\%$ in soil. If several spectral ranges are used (for example, 2.3 and 3.2 μm), the analyzer

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