

INVESTIGATION OF THE OIL-PRODUCTS SOLUBILITY IN WATER: QUALITATIVE COMPOSITION AND QUANTITATIVE LIMITS OF THE OIL–WATER MIXTURES

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Abstract. Gasoline–water mixtures have been investigated using UV-spectrophotometry. It was found that such mixtures can be characterized with two absorption bands. The first one is located within wavelengths from 180 to 230 nm and the second is located within 240–280 nm. The first absorption band is very intense and cannot be used for any analytical determination while the second one exhibits distinct dependence on the gasoline concentration. Calibration diagrams have been built in the coordinates: optical density vs gasoline concentration for the UV-light absorption peak at 260 nm. Assumption on the qualitative composition of the gasoline–water mixtures has been made basing on the pattern and the peaks distribution along the light absorption spectra. It has also been found that the maximum concentration of the relatively soluble gasoline components reaches approximately 0.35 g/l. However, higher concentrations can be achieved at longer contacting between gasoline and water.

Keywords: oil–water mixtures, UV-spectrophotometry, qualitative composition, quantitative limits.

1. Introduction

Oil-products are very dangerous and toxic pollutants of water. Annual world discharge of oil-products reaches 1.5–2.5 million tons [1]. They contaminate river, sea and ocean water and come from various industrial wastewater discharges, tanker ballast waters exchange and other anthropogenic sources [2]. Severe local contamination always occurs at tanker incidents, oil pipelines ruptures and other technical accidents.

Accurate assessment of negative effect of the oil-products contamination is impossible without reliable and accurate methods of analytical determination of the oil-products concentration.

There are many well-known analytical methods, which have been embodied in various types of analytical equipment produced commercially. Infrared spectroscopy, fluorescent spectroscopy, gas and gas-liquid chromatography can be mentioned as such accurate and reliable methods of the oil product content determination. However, these methods require long and complicated samples preparation including extraction of oil-products from water (like infrared photometry or fluorescence methods) and/or some expensive and rather large lab equipment, which can be used only in a stationary laboratory (like gas or gas-liquid chromatography) [3–5].

Field or express analysis require faster and simpler method of the oil-products content determination. This method can ensure lower accuracy but requires shorter time and less equipment.

We propose an express method for analytical determination of the oil-products content in water. It requires quite simple lab equipment and does not involve extensive samples preparation operations. This method can be realized in a simple lab (potentially even in a mobile one) providing possibility of on-a-spot determination of water contamination with oil-products.

2. Oil–water mixtures: solubility, composition and spectrophotometry investigation

Most oil products and water are considered as non-soluble in each other. It is well known that gasoline, oils, grease or diesel fuel can form thin film spreading wide on the water surface. This contamination results in many negative ecological effects: oil film on the water surface blocks up normal gas exchange with atmosphere lowering oxygen content in water. This leads to anoxaemia and suffocation of fish and other water organisms. Water birds suffer of the feathering dirtying, try to clean themselves, swallow oil from their feathering and die of poisoning. Same situation also happens to other organisms including mammals, which can eat birds, fish or other organisms perished after oil-products poisoning.

This kind of pollutants may also stay captured in the shore and offshore area soils for years and be released periodically because of weather and/or sea condition changes.

Oil and water were considered as almost completely dissoluble components. However, it was recently found that long-term contacting of water and oil may result in dissolution of some oil-components in water. Solubility of crude oil in water can reach 0.2–1.9 mg/l at the contacting time of 120 h. Solubility of diesel fuel at the same conditions can reach 0.8 mg/l.

Gasoline is even more dissoluble since it contains relatively higher amount of the aromatic compounds. It was found that aliphatic gasoline compounds concentration can reach 11.9 mg/l and concentration of aromatic compounds can reach 134 mg/l.

It is known that some classes of relatively better dissoluble compounds (methyl and polymethylbenzenes, etc.) are present in the oil products, especially in the high-octane gasoline [3, 6]. Some small amount of these compounds can be dissolved in water and contaminate deep-water ecosystems as well as surface ones. Such contaminated water can travel a long distances (especially with the river flow) and distribute pollutions over long range. Naturally, express control and determination of such a contamination would require fast and mobile analytical methods and laboratories, which would be able to follow the contaminated water spot.

So, necessity of elaboration of some relatively simple but still reliable analytical techniques to determine oil-product content in water is obvious.

It is known that many aromatic compounds can actively absorb light in the closer UV range [7]. This can be used for direct UV-spectrophotometry determination of their concentration in water. This analytical method would not require intense samples preparation and needs simple analytical equipment.

This assumption was verified through recording of UV-spectra of diluted water-gasoline mixtures. An ordinary A-95 gasoline was used as a test oil compound and its concentration in water was ranged from 0.03 to 0.35 g/l. All the spectra were recorded immediately after preparation of the solutions using standard LOMO SF-26 spectrophotometer. Typical UV spectrum of the gasoline-water system can be seen in Fig. 2.1

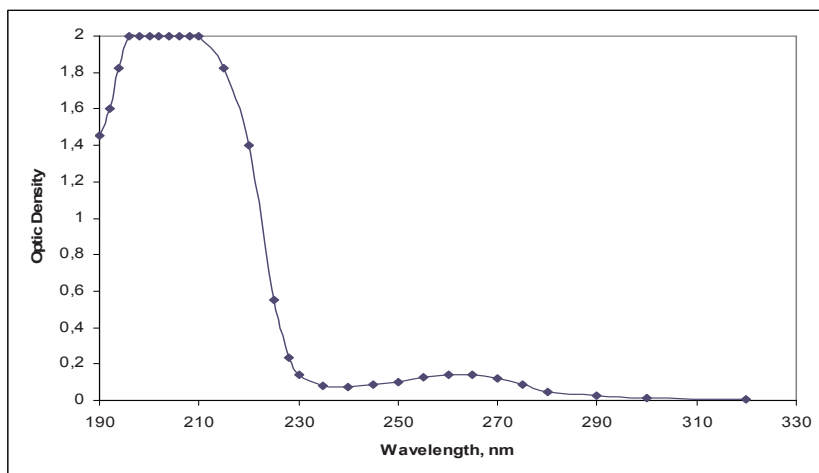


Fig. 2.1. Typical UV spectrum of the gasoline-water system.

One can see a band of a very intense light absorption located around wavelength 230 nm and further to the short-wave part. Another absorption band is located between 240 and 280 nm. The first band is very intense and almost independent from the gasoline concentration (non-analytic light absorption peak). Intensity of light absorption within the second band was found dependent on the gasoline concentration (analytic absorption peak). This absorption band is enlarged in Fig. 2.2.

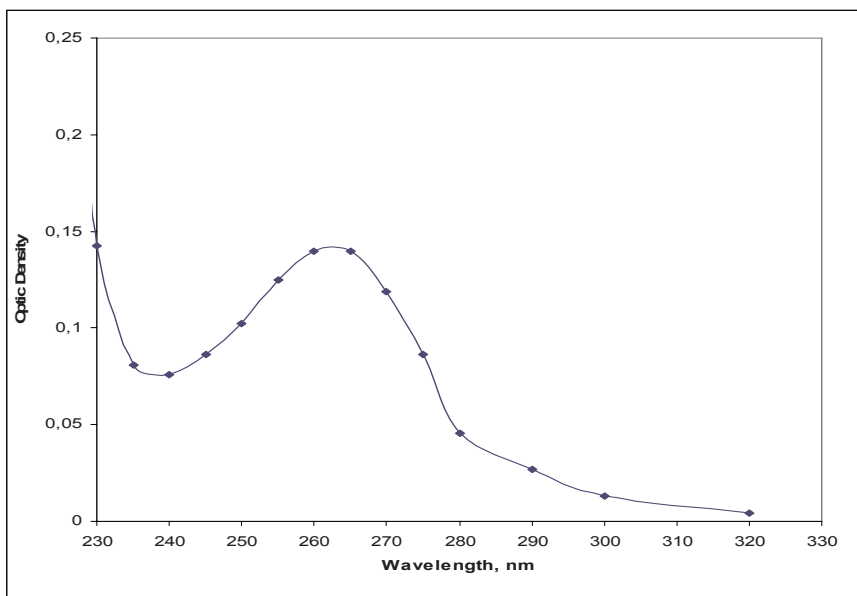


Fig. 2.2. Part of the gasoline–water UV-spectrum with the analytical adsorption peak found.

It is seen that the maximum light absorption is registered at the wavelength 260 nm. This peak can be used to build a calibrating diagram connecting optical density of a solution (D) and concentration of gasoline (c). This dependence was found linear and corresponding to the calibrating equation $D = 0.315 c + 0.0112$ (see Fig. 2.3). It fits experimental values with the pair correlation coefficient 0.97 or higher along all above mentioned range of the gasoline concentrations and can be used for express UV-spectrophotometry determination of the gasoline content in water.

Then the water-gasoline spectrum pattern was compared to typical spectra of various aromatic compounds [7, 8]. This class of organic substances can be found in gasoline and they actively absorb UV radiation. As a result, we have found that a spectrum and its pattern was very similar to our experimental results (see Fig. 2.4). This is a spectrum of 1,3,5-trimethylbenzene and it practically agrees with an experimental light absorption pattern recorded near 260 nm.

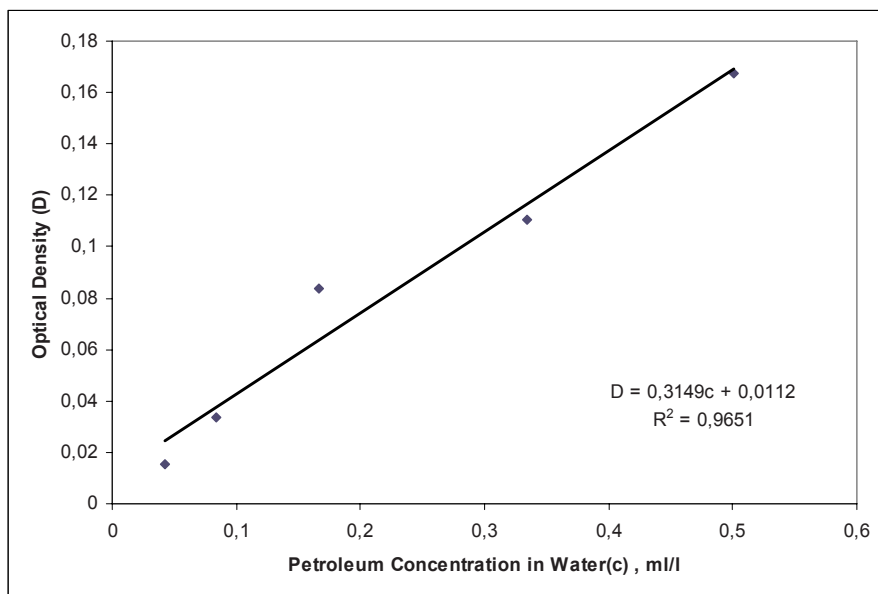


Fig. 2.3. Calibrating diagram for determination of gasoline concentration through UV-light absorption at 260 nm.

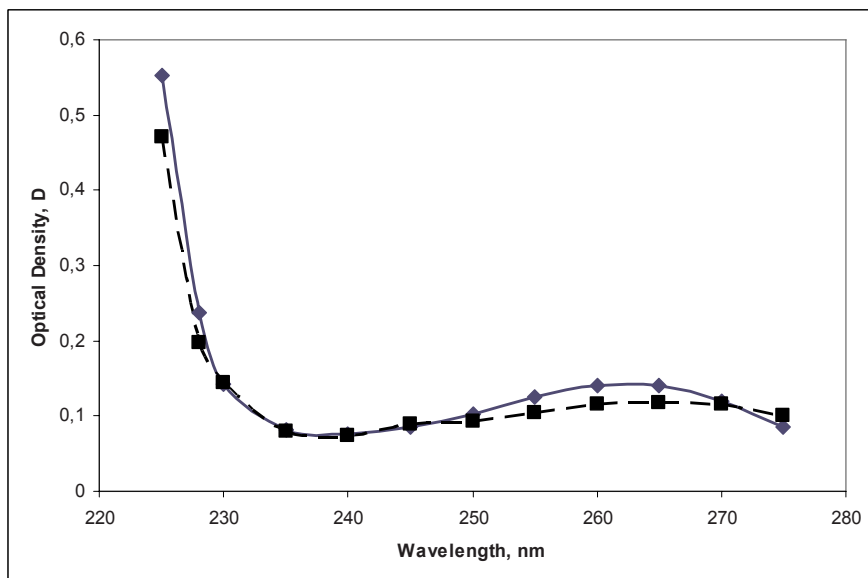


Fig. 2.4. UV spectra of the gasoline-water solution (solid line) and 1,3,5-trimethylbenzene (broken line) [7].

Therefore, we suppose that 1,3,5-trimethylbenzene or its close homologues can be those relatively well-dissoluble gasoline compounds, which form pattern of the analytical absorption peak for the water-gasoline mixtures. It is also known that aromatic compounds determine higher octane number of the high performance motor fuel and in fact they are present in the high-octane gasoline. This result can be used for express analytical determination of the oil-compounds content in water objects.

Using this method we have also determined quantitative limits of the gasoline–water solution. It was found that optical density of the light absorption band 260 nm reaches maximal value at the gasoline concentration of 0.35 mg/l. Further adding of gasoline did not lead to the changes in optical density. This result proves that a solution of A-95 gasoline in water can reach maximal concentration of 0.35 mg/l. Higher concentration can potentially be reached at longer gasoline/water contacting time.

3. Conclusions

An original UV-spectrophotometry method can be recommended for the test determination in order to investigate its reliability in analytical determination of the oil contamination of water. It is simpler and less expensive comparing to other analytical methods. However, its usage is limited by high-octane motor fuels containing 1,3,5-trimethylbenzene or its homologues. These compounds are in fact registered through 260 nm UV light absorption band. Maximal concentration of 1,3,5-trimethylbenzene or its homologues in water is 0.35 mg/l are reached after the short contacting time.

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