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METHODS OF ANALYSIS

NEW METHODS FOR ATOMIC-ABSORPTION DETERMINATION OF METALS IN AVIATION AND AUTOMOTIVE GASOLINES

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Methods were developed for direct atomic absorption determination of lead and lithium as components of antiknock additives in aviation and automotive gasoline at concentrations in the ranges of 100–1700 (lead) and 2.5/0.25-100 (lithium) mg/dm^3. The conditions of atomization of the sample solutions and calibration solutions and elimination of the effect of the matrix of the analyzed samples on the results were achieved by suitable dilution of the samples and by including aliquots of solutions simulating the composition of gasolines prepared from individual high-purity hydrocarbons in the composition of the reference solutions and calibration solutions. The methods are characterized by high precision, are simple to use, and can be recommended for quality control and identification of gasoline.

Key words: *aviation gasoline, automotive gasoline, antiknock additives, tetraethyllead, lithium carboxylates, atomic absorption spectrometry, matrix effects.*

The requirements for the quality and environmental safety of fuel and lubricant materials (FLM) are constantly increasing, and the range and list of components involved in them are escalating. Here, it is necessary to improve the reliability of the results of ensuring that the quality of petroleum products meet the requirements of regulatory documents and the requirements of their production technology, including the development and introduction of new and modernized fuels and lubricants for use in technical equipment. In this connection

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special urgency applies to the improvement of methods for controlling the quality petroleum products, investigating their quality, and identifying them.

The need to improve the reliability of information about the composition of petroleum products and the actual values of their quality indices and also the productivity of the production processes gives rise to the expediency of expanding the list of physical and physicochemical methods for investigating the composition of the materials.

By expanding the application fields of these methods in order to study and identify the composition of petroleum products it is possible to reach more reliable conclusions about the agreement of their actual composition with the composition declared by the manufacturer and to make decisions on the possible further use of petroleum products and/or the need to take measures aimed at restoring their quality. The use of highly informative methods for analyzing the composition of a substance, including those available in microquantities, is particularly important when carrying out chemical studies of equipment failures, associated with the use of fuels and lubricants [1].

Some of the most common objects of research in the implementation of quality control and identification of fuels and lubricants are gasolines – aviation gasoline produced according to standards GOST 1012-2013 and GOST R 55493-2013 and automotive gasoline produced according to GOST 32513-2013, GOST R 51866-2002 and GOST 51105-97. The quality indicators of gasoline, which are standardized by the specified documentation and the Technical Regulations of the Customs Union "On requirements for automobile and aviation gasoline, diesel and marine fuel, jet , and fuel oil" (TR TS 013/2011), include the content of components that have antiknock activity and determine the actual level of detonation resistance of gasolines, the grade of aviation gasolines based on a rich mixture, and the applicability of gasolines in technical items. Thus, according to the requirements of GOST 1012–2013, the content of tetraethyllead (TEL), which is the most effective antiknock agent, should not be more than 2 g/kg in the composition of B-92 gasoline, not more than 2.5 g/kg in B-91/115 gasoline, and not more than 0.53 ml/dm^3 (not more than 0.56 g/dm^3) in Avgas 100 LL gasoline (according to GOST R 55493–2013).

The requirements of modern regulatory documents for the quality of automotive gasoline prohibit the presence of metal-containing additives. (Trace quantities of metal compounds at the level of detection limits of the applied control methods are permitted.) However, a feature of the wording of the provision relating to additives containing manganese, lead, and iron in the text of TR TC 013/2011 and GOST 32513–2013 and the presence of standards for the content of only these metals in other regulatory documents for automotive gasoline allow the formal possibility of adjusting the octane number of gasoline and preparing separate batches of high-octane gasoline under off-plant conditions with the use of alternative antiknock agents based on metal compounds not listed in the regulatory documents for automotive gasoline. Such antiknock agents include compounds of certain transition metals, including compounds of potassium, sodium, cesium, and lithium [3, 4].

In view of the solubility of the lithium salts of various organic acids in hydrocarbon media over a wide range of temperatures and also the industrial availability of the components for the production of lithium-containing compounds (lithium hydroxide and organic acids, higher carboxylic and salicylic acids), these compounds have been used in the composition of the additives Likar (a mixture of a lithium salt and polyethyleneglycol ether) and Liton (a solution of a lithium salt in acetone), developed at Kazan State Technological University between 2000 and 2005, which have fairly high antiknock efficiency [5-9].

Owing to the ban on the use of metal-containing antiknock agents in automobile fuels the interest in lithium-containing additives in the subsequent period practically disappeared, but it has now re-emerged.

Research aimed at developing methods for the production of new fuel-soluble lithium compounds, such as high-molecular-weight acid alkenylalkanedioates of alkali metals has resumed [10]. In addition, polyalkylalkanoates and also lithium alkylsalicylates have been proposed as additives in fuel-oil compositions for two-stroke gasoline engines [11, 12], which have significant prospects for use in modern technology.

The need for control over the metal content of fuels envisaged by the regulatory documents for fuels is due to the potential effect of the respective compounds on the physicochemical and operational properties of the fuels [13]. The problems accompanying the use of lithium-containing antiknock agents in automotive gasoline include the hydrolytic instability of the lithium salts, their leaching from the composition of gasoline during contact with water, and the conversion of lithium carboxylates into a dry residue during atmospheric distillation of the gasoline, which can lead to the formation of deposits in the intake line of the fuel supply system, as well as deterioration in the strength characteristics of the elastomers. In addition, according to thermogravimetric investigations [14], the product of thermal transformations of lithium isoalkylcarboxylates at temperatures above 720 ° C is thermally stable lithium carbonate, which can form deposits on the surface of parts of the cylinder-piston system of the engine, as well as in the exhaust and catalytic neutralization system, including the surface neutralizers and sensors of lambda probes. Carriers for lithium antiknock agents are not known.

A flame-photometric method was previously developed to determine the lithium content of automotive gasoline [15, 16]. It was noted that direct determination of lithium in an organic matrix, which automotive gasoline is, is difficult because of its effect on the stability of the employed low-temperature propane–butane/air flame. For this reason the analytical procedure included a stage of extraction of the lithium compounds into the aqueous phase by treating the gasoline sample with hydrochloric acid solution with separation of the phases and additional washing of the gasoline phase with water.

The lithium in the combined aqueous phase was determined with the use of calibration solutions prepared from an inorganic salt of potassium – its chloride. The sensitivity of determination of the lithium amounted to 3 mg/dm^3 with a relative error of not more than 12%. Other known and abundant methods for determination of lithium, including atomic absorption methods, apply to the analysis of aqueous solutions [17] and are not suitable for the investigation of the composition of fuels.

The lead content from antiknock tetraethyllead in aviation gasoline of grades B-92 and B-91/115, produced in accordance with the GOST 1012 standard, is determined according to the GOST 28828-90 [18] and GOST 13210-72 [19] standards, and in Avgas 100 LL gasoline produced in accordance with GOST R 55493–2013 it is determined according to the GOST 28828–90 and foreign standards [18, 21–25]. The content in tetraethyllead in aviation gasoline is calculated from data obtained by the indicated methods. In addition, there are domestic standardized X-ray fluorescence methods for the determination of lead in gasoline in a wide range of concentrations that are not included in the regulatory documents for aviation gasoline, and are set out in the standards GOST R 54278-2010 [23] and GOST 33899-2016 [24] and are identical with the standards in [25, 26]. The characteristics of the indicated standardized methods are presented in Table 1.

The reliability of the results obtained by the indicated methods [27] is determined by realization at the sample preparation stage of procedures that ensure that there are consistent forms of the analyte and of the matrix containing them in the solution of the sample being analyzed and the calibration solutions in related methods [18, 22] and also by titration in an aqueous medium of solutions of the products from acid mineralization of the samples in absolute methods [19-21. However, the complexity of the respective operations and the need to use a significant amount of solutions of the reagents give rise to long duration and difficulty of determination.

In relative methods based on the use of X-ray fluorescence spectroscopy [23–26] and not involving sample preparation agreement between the composition of the analyte forms in the sample and in the reference samples is only guaranteed when substances containing lead in the form of a compound present in aviation gasoline, namely tetraethyllead, are used as reference samples.

The corresponding Russian reference samples (reference samples with compositions that have been reliably established and legally certified) are not released, and foreign reference samples for the composition of lead compounds in the form of tetraethyllead in leaded gasoline are not readily available. The possibility of using the indicated methods in the analysis of aviation gasoline in reference samples prepared on the basis of tetraethyllead and also lead naphthenate involves the need to establish the exact content of lead in the composition of the corresponding industrial products by, for example, a titrimetric method.

Here the high toxicity of tetraethyllead, which is a class I hazardous substance [28, 29], excludes the possibility of carrying out appropriate analyses in laboratories not accredited to work with such substances, which include most laboratories for quality control and research on the composition of fuels and lubricants. In addition, the different nature of the chemical bonds in the molecules of lead naphthenate as reference sample and in the molecules of the organometallic compound of the sample being analyzed can lead to erroneous results [30].

Use of the method for determination of lead in aviation gasoline included in the list of test methods in GOST R 55493-2013 by the atomic absorption method according to the IP 428:2004 standard [22], which provides for conversion of lead compounds from the analyzed sample and reference samples into a single form, is actually illegal, since the specified method is intended for the determination of lead in gasolines at concentrations in the range from 5 to 25 mg/dm^3 (from 2.5 to 10 mg/dm^3 in the 2015 edition of the standard), corresponding to the previous standard GOST 2084-77 for the content of this element in automotive gasoline(not more than 13 mg/dm^3) and not corresponding to the content for aviation gasoline. Thus, the upper limit of the range of lead concentration in aviation gasoline produced in accordance with GOST 1012, calculated on the basis of the standard for the content of tetraethyllead (up to 2.5 g/kg) and the formula content of lead in the composition of this compound (64.11%), is at the level of 1600 mg/dm^3, which is significantly higher than the lead content of automotive gasoline. The rapid methods for determination of lead [31, 32] apply automotive gasoline and are semi-quantitative.

Thus, it can be concluded from analysis of the presented data that there are at present no simple and high-performance methods that also give reliable results in quantitative methods for determining the content of metals from the composition of antiknock agents added to the gasoline: lead from the tetraethyllead and ethyl liquid, which is a standard antiknock agent in aviation gasoline, and lithium from alternative antiknock agents in automotive gasoline. It should be noted that determination of the content of the metals in petroleum fuels is an important stage of the procedures for assessing compliance of their quality with the requirements of the regulatory documents and their relevance to specific subgroups of gasolines and identifying substandard products. In addition, monitoring the lead content of aviation gasoline is an indirect way of accounting for the consumption of highly toxic ethyl liquid in order to ensure the environmental safety of the production and use of gasoline.

In accordance with this the aim of the present investigation was to develop new methods for quantitative determination of the contents of lead in aviation gasoline and of lithium in automotive gasoline.

Atomic absorption spectrometry, which is a highly sensitive, selective, and productive method free from spectral interference for determining the content of metals from the composition of their various compounds present in oil products and can be performed on equipment that is widely available on the market [33], was

Table 1

Normative document	Concentration of lead, mg/dm^3	Detection method	Sample preparation
GOST 28828-90 [18]	5–3000	Spectrophotometry, complex with 4-(2-pyridazo)resorcinol or sulfarsazene (520 or 500 nm)	Extraction of tetraethyllead into aqueous solution of iodine monochloride (ICl), treatment of partial mineralization product with solutions of ammonia and sodium thiosulfate (removal of excess ICl); aqueous calibration solutions
GOST 13210-72 [19]	From less than 200 to more than 800	Titrimetry, Na-EDTA, indicator xylenol orange	Decomposition of tetraethyllead by boiling with hydrochloric acid, evaporation of extract, decomposition of organic residue with nitric acid and hydrogen peroxide
ASTM D3341-05 (2011) [20], IP 270:1996 (R 2004) [21]	26-1300		Extraction of tetraethyllead into ICl solution, evaporation of extract, oxidation of organic residue with concentrated nitric acid
IP 428:2004 [22]	5-25 (2.5-10 in 2015 edition)	Atomic-absorption spectrometry	Mineralization of tetraethyllead in organic solvent by treatment with iodine solution, stabilization of solution of reaction products with quaternary ammonium salt, calibration solutions based on lead chloride with similar treatment
GOST R 54278-2010 [23], GOST 33899-2016 [24] ASTM D5059-07 [25], IP 228:2004 [26]	2,6-1320	X-Ray fluorescence spectroscopy	Sample preparation not required. Calibration solutions based on tetraethyllead or lead naphthenate in isooctane

chosen as method to determine the content of the metals in aviation and automotive gasoline. The procedures for optimizing the conditions of determination, calibration, and treatment of the results from analysis of the metal contents in petroleum products are described in the standard [34].

During development of the methods the following features were considered to be the main objects of the investigation:

1) Exclusion of mineralization by acid decomposition of the samples from the determination procedure;

2) Creation of identical conditions for atomization of the solutions of the sample and of the reference samples by obtaining the same chemical form of analyte for the sample and for the reference samples as the composition of its compound and also the composition of the matrix in the medium containing the analyte.

Solution of these problems ensures reliable results for determination of the analytes by methods based on the use of calibration dependences of the analytical signal on the concentration of the analyte in the reference samples, including atomic absorption spectrometry [35], and can be regarded as conditions (conditions 1 and 2) for the production of such results by the newly developed methods.

The investigations were conducted on a PerkinElmer PinAAcle 500 double-beam atomic-absorption spectrometer with Syngistix software and flame atomization of solutions of the gasoline samples being analyzed and calibration solutions.

The need to fulfill condition 1 determines that the analysis must be conducted in organic solvents and, consequently, with the use of standard samples or reference samples that are soluble in such solvents for preparation of the calibrated solutions. Here the use of CONOSTAN Oil Analysis Standards of SCP SCIENCE standard samples, soluble in most organic solvents and designed for determination of the content of metal compound impurities in petroleum products, as standard samples in order to fulfill condition 2, must be excluded when developing a method for the atomic absorption determination of lead in aviation gasoline on account of discrepancy between the nature and energy characteristics of the chemical bonds of the analyte in the molecules of its compound in the sample and in standard sample. Conditions 1 and 2 are fulfilled in standardized atomic-absorption methods for determination of lead in automotive gasoline for concentrations from 2.5/5 to 25 mg/dm^3 according to GOST 32350-2013 and ASTM D3237-12 [37] and also according to standard IP 428:2004 [22]. This made it possible to use these methods as prototypes in the development of a method for the determination of lead in a matrix of similar composition, which aviation gasoline is.

It is proposed that the production of identical forms of analyte in solutions of the samples and of the reference samples in the method for determination of lead in aviation gasoline should be carried out in a way similar to that described in the prototype methods – mineralization in organic matrixes by treating an aliquot portion of the sample being analyzed with a solution of iodine according to the scheme:

$$Pb(C_2H_5)_4 + I_2 \rightarrow Pb(C_2H_5)3I \rightarrow Pb(C_2H_5)_2I_2 \rightarrow (Pb(C_2H_5)I_3 \rightarrow PbI_4) \rightarrow PbI_2 + C_2H_5I$$

A solution of iodine was also added to the calibrated solutions based on lead chloride. The formed iodine-containing compounds were stabilized by reaction with a quaternary ammonium compound (tricaprylmethylammonium chloride – Aliquot-336), a surfactant used also as a phase-transfer catalyst, with simultaneous addition of a 10-fold dilution of the sample and the initial reference solutions.

Here in order to harmonize the analytical procedures of the developed method and the prototype methods, the type of solvent used in the latter and the concentrations of the calibration solutions were left unchanged. Accordingly, lead chloride was used as substance for preparation of the calibration solutions, and methyl isobutyl ketone was used as solvent; the concentrations of lead in the working calibration solutions were 0.53, 1.32, and 2.64 mg/dm^3. In addition, in order to extend the limits of the range of determined lead concentrations additional calibration solutions with concentrations of 3.4 and 0.24 mg/dm^3 were prepared to determine lead contents in a range of up to 1700 mg/dm^3 and to determine impurity concentrations of tetraethyllead respectively.

To bring the lead content of the analyzed solutions into line with the concentration of the calibration solutions in the preparation of the sample, it was proposed to introduce an additional stage – dilution of the gasoline samples with methyl isobutyl ketone before mineralization in the organic matrices as medium. Taking account of the typical level of lead content for aviation gasoline and according to the results of the investigations, the optimal value for the degree of dilution of the samples is 25 for Avgas 100 LL gasoline and 50 for B-91/115. During investigation of the composition of an aviation gasoline of unknown grade the degree of dilution is chosen so that the optical density recorded during atomization of the solution obtained as a result of the realization of both types of sample preparation lies in the range of optical density values recorded during atomization of the calibrated solutions.

To ensure that the compositions of the matrix (base) of the solutions of the analyzed samples of fuels and the solutions of the reference samples correspond the highly sensitive methods being developed must provide for the addition of an aliquot of the product, with composition as close as possible to the composition of the analyzed sample and without compounds of the determined elements, to the calibration solutions and the reference solution. Such product is regarded as a blank sample and as a component of the reference solution the optical density of which is taken as zero during photometry. In the prototype methods unleaded automotive gasoline is used as a blank. However, due to the fundamentally possible introduction of trace quantities of metal compounds into the petroleum products during transportation and storage, it is not possible a priori to consider unleaded gasoline to be free from lead compound impurities.

In accord with this and also taking account of the poor availability in laboratory practise of the industrial hydrocarbon mixtures that are basic in the production of commercial aviation gasolines and the differences in the composition of automobile and aviation gasolines, as blank sample for addition to the composition of the calibration solutions and the reference solution, it is proposed to use a simulator of the composition of aviation gasoline (model aviation gasoline) as a mixture of the major hydrocarbon components of commercial aviation gasoline in the form of commercially available high-purity chemical reagents.

Taking account of information on composition of aviation gasoline [38, 39], a mixture of isooctane, toluene, cyclohexane, and n-heptane of reagent grade at concentrations of 70, 20, 5, and 5 vol.% respectively was used as simulator. Despite the high total degree of dilution of the sample, being analyzed, the use of a simulator of the composition of aviation gasoline as blank sample and its addition to the calibration solutions as well as to the pure solvent (methyl isobutyl ketone), in order to obtain the reference solution it is necessary to eliminate the effect of solutions of the analyzed sample present in the composition of the solutions and the working calibration solutions of additional components (iodine and stabilizer Aliquat-336) on the photometric results. The obtained graph for the concentration dependence of the optical density values recorded during atomization of the calibration solutions is linear at lead concentrations in the range from 0.24 to 3.4 mg/dm^3; the range of determined lead concentrations in aviation gasoline is from 120 to 1700 mg/dm^3.

The concentration of lead in the analyzed solutions was calculated from the optical density values recorded during their atomization using the software of the spectrometer according to the calibration curve. The lead content of the analyzed aviation gasoline samples was calculated according to the formula:

$$C_{\text{Pb-avg}} \to C_{\text{Pb-sol}} \cdot n \cdot 10$$

where $C_{\text{Pb-sol}}$ is the concentration of lead in the analyzed sample solution, mg/dm^3; n is preliminary dilution of the aviation gasoline; 10 is the degree of dilution of the analyzed solutions at the stage of mineralization of the diluted sample of gasoline.

For a metrological examination of the method, solutions of the commercial antiknock additive AvTEL–TEL-B containing tetraethyllead, manufactured by Innospec Ltd., were prepared on the basis of aviation gasoline obtained from a gasoline manufacturer (a mixture of the hydrocarbon components of aviation gasoline), with five concentration levels in the specified range of values. The prepared samples were analyzed according to the procedure of the method. The metrological characteristics of the method were determined according to GOST R ISO 5725-1-2002 [40] and RMG 61-2010 [41]. The results from calculation of the metrological characteristics are presented in Table 2.

The accuracy of the results was confirmed by comparison with the results from analysis of identical samples according to GOST 28828–90 [18]. The results from determination of the lead content of the aviation gasoline samples by the developed and standard methods are presented in Table 3.

From the obtained data it possible to characterize the developed atomic absorption method for determination of lead in aviation gasoline as providing reliable results with high precision.

During development of the atomic-absorption method for determination of the lithium content in automotive gasoline the solubility of samples of automotive gasoline was first investigated in a series of solvents commonly used in atomic spectrometry: methyl isobutyl ketone, a purified kerosene fraction of oil refining in the form of commercial solvent Premisolv ICP Solvent (SCP Science) not containing impurities of metal compounds, toluene, and isopropyl alcohol. The formation of true solutions was observed with all the above-mentioned solvents. Here, the best oxidative character of the flame used to atomize the analyzed samples and calibration solutions was obtained with methyl isobutyl ketone, Premisolv solvent, and isopropyl alcohol. On account of low toxicity, commercial availability, and low cost isopropyl alcohol was chosen as a solvent in the development of a generally accessible method.

Photometry of solutions of samples of commercial automotive gasoline of ecological class K5 in isopropyl alcohol was used to study the possibility that the results from determination of lithium could be affected by characteristics of the composition of the automotive gasoline. In addition, in order to avoid a preliminary analysis of commercial gasoline for the absence of metal compounds as impurities, solutions of gasoline simulating the composition of commercial gasoline, prepared from individual hydrocarbons in the form of reagents of chemical purity grade, were subjected to atomization.

With due regard to the results from investigations of the detailed hydrocarbon composition of the automotive gasoline samples by capillary gas chromatography according to GOST 32507–2013 [42], it is proposed to use a solution containing isooctane, toluene, cyclohexane, and n-heptane at concentrations of 50, 30, 10 and 10 vol.% respectively to simulate the composition of automotive gasoline. Photometric measurements were made on solutions of commercial automotive gasolines and simulated gasoline at a concentration of 2 vol.%, which corresponds to 50-fold dilution.

In addition, solutions containing 10, 20, and 50 vol.% of gasoline, which corresponds to 10-, 5-, and 2-fold dilution, were used to study the possibility of detecting the presence of additives and, accordingly, determining low levels of lithium. Isopropyl alcohol without additions was used as reference solution. During photometric investigation of the solutions, the nature of the flame was established, and the optical density values of solutions of commercial and model gasolines were recorded (Table 4).

Table 2

Determined element	Concentration of element, mg/dm^3	Repeatability indices, mg/dm^3		In-laboratory precision index, mg/dm^3	Accuracy index, mg/dm^3
		standard deviation of repeatability	repeatability limit	standard deviation of in-laboratory precision	absolute error limits
Pb	from 120 to 1700	$0.043x–1.371$	$0.118x–3.792$	$0.033x–1.568$	$0.065x–3.079$
Li	from 2.5 to 100 inc	$0.022x+0.053$	$0.060x+0.148$	$–0.0001x^2+0.021x–0.044$	$–0.0001x^2+0.04x–0.018$

Table 3

Aviation gasoline sample number	Lead content, mg/dm^3	
	by developed method	by GOST 28828-90 method
1	250+20	235+18
2	435+28	418+31
3	754+70	709+42
4	1143+103	1215+158

Table4

Concentration of commercial automotive gasolines and gasoline simulator, vol. %	Optical density, arb. units
2	0
10	0
20	0.0015-0.0025
50	0.0034-0.0049

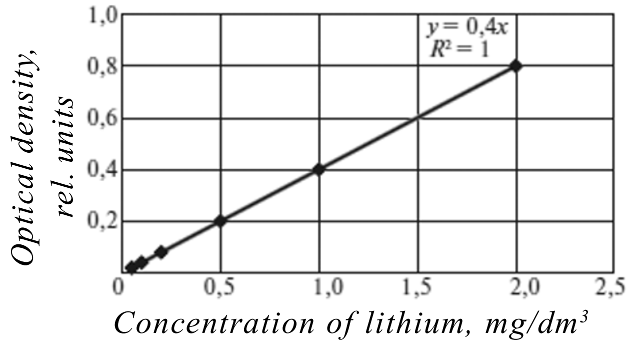

Figure. Dependence of the optical density on the concentration of lithium in the calibration solutions

The data in Table 4 indicate that the optical densities during atomization of the solutions of gasoline with concentrations of 2 and 10 vol.% do not differ from those for the reference solution. Analogous conclusions apply to the nature of the flame of the solutions. During atomization of solutions of automotive gasoline with concentrations of 20 and 50 vol.% nonzero values were obtained for the optical density, and the flame moreover acquired reducing character.

Together with the absence of additional mineralizing and stabilizing components the obtained results have made it possible to avoid the addition of aliquots of a blank sample (gasoline simulator) to the calibration solutions and the reference solution during analysis of samples diluted by 10, 50, or more times and also to use isopropyl alcohol without additions as reference solution during analysis of gasolines with a appropriate concentration of lithium-containing additives. With a sample dilution factor of not more than 5, which is necessary when determining low concentrations of lithium from the composition of additives used for minor correction of the octane number, it is proposed to add aliquots of simulating gasoline at the appropriate concentration to the composition of the prepared calibration solutions and the reference solution based on isopropyl alcohol.

As reference samples for the atomic absorption determination of lithium in automotive gasoline, with due regard to the composition of the active component of the lithium-containing antiknock additives (the lithium salts of organic acids), in order to ensure that the conditions for atomization of the sample solution and calibration solutions during preparation are identical it was proposed to use a standard CONOSTAN sample (concentration 5000 ìg /g) for the composition of the organic lithium salt in the form of its cyclohexyl butyrate. By studying the concentration dependence of the optical density of the calibration solutions, prepared from the indicated standard sample in isopropyl alcohol, it was possible to establish linearity for the calibration graph in the range of lithium concentrations from 0.05 to 2 mg/dm^3; the detection limit for lithium is 0.005 mg/dm^3. The dependence of the optical density recorded during atomization of the lithium calibration solutions on their concentration is shown in the figure.

On account of the obtained data and also of the information on the concentration of lithium-containing additives in automotive gasoline, ranging from 20 to 100 mg/dm^3, a universal value of 50 for the indicated range of concentrations was chosen as optimum value for the degree of dilution of the analyzed gasoline samples. Here, the range of determined values for the concentration of lithium in automotive gasoline is between 2.5 and 100 mg/dm^3. With fivefold dilution of the analyzed gasoline the lower limit of the range of determined concentrations of lithium amounts to 0.25 mg/dm^3.

The obtained results were used as the basis of a method for determination of lithium in automotive gasoline. During development of the method a calibration solution with a lithium concentration of 50 mg/dm^3 was first prepared from a standard sample, after which a series of calibration solutions with concentrations of 0.05, 0.1, 0.2, 0.5, 1, and 2 mg/dm^3 were prepared by dilution with isopropyl alcohol. If there is information about the presence of lithium-containing antiknock agents in the composition of the gasoline being investigated, the sample taken from its volume is diluted 50 times with isopropyl alcohol. If it is necessary to determine lithium at a concentration of more than 100 mg/dm^3, the dilution ratio of the analyzed gasoline samples is increased; if it is necessary to detect lithium at a concentration of less than 5 mg/dm^3, the samples are diluted five times. In this case aliquots of the simulator solution of the automotive gasoline are added to the calibration and reference solutions so that the concentration corresponds to the degree of dilution of the sample.

The lithium content of the analyzed samples of automotive gasoline (mg/dm^3) was calculated according to the formula:

$$C_{\text{Li-gas}} \rightarrow C_{\text{Li-sol}} \cdot n$$

where $C_{\text{Li–s-s}}$ is the concentration of lithium in the analyzed solutions, mg/dm^3; n is the degree of dilution of the analyzed sample of gasoline, amounting to 50 or more or not more than 5.

The result of the analysis was taken to be the arithmetical mean value of the concentration of lithium in the sample, obtained from two successive determinations.

The metrological characteristics of the method for determination of lithium in auto gasoline are presented in Table 2. The accuracy of the results was confirmed by analyzing prepared solutions of a standard sample of the composition of the lithium salt in the gasoline simulator. The developed methods form the basis for the organization standards of the FAU “25 State Research Institute of Chemotology of the Ministry of Defense of Russia.”

With respect to the specific requirements for the quality indicators for aviation and automotive gasolines, the presence in a gasoline sample of unknown origin of lead impurities from the composition of its compounds in the corresponding concentration range can be considered as an identifying attribute indicating that the gasoline belong to the aviation gasoline subgroup in terms of GOST 26098–84. The presence of lithium in automotive gasoline indicates that the gasoline does not meet the requirements of the regulatory documents. Lead at an appropriate concentration and lithium can regarded as elements indicating that gasoline samples belong to specified subgroups of the fuel group for engines with positive ignition, while highly informative methods for determination of these elements in gasoline can be used for identification of the relevant petroleum products.

Introduction of the developed methods for the determination of lead in aviation and of lithium in automotive gasolines will prevent the use of fuels that do not meet the requirements of regulatory documents in technical facilities and can therefore be considered as a factor in ensuring the safe operation of aviation and automotive equipment.

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