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Solid Phase Microextraction Of 1,1-Dimethylhydrazine With Derivatization By Acetone

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Rocket-space activity in Kazakhstan holds one of the leading places among the sources of contamination of environmental objects in the most parts of the country. 1,1-Dimethylhydrazine, used as the main component of rocket fuel, gets into the soil and water through falling of separating parts of rocket-carriers. Due to its high reactivity, 1,1-dimethylhydrazine is involved in many reaction of oxidation, reduction, etc. immediately after falling of separating parts of rocket-carriers. Many of these reactions causes the formation of toxic products of 1,1-dimethylhydrazine transformation, most of which have the higher toxicity than the initial compounds [1]. However, despite the fact that 1,1-dimethylhydrazine is decomposed in the environment almost completely, it was found in soils of old fall places, which had not been in use for many years. That phenomenon was explained by the author of [2], who found that products of 1,1-dimethylhydrazine transformations are able to form 1,1-dimethylhydrazine through various reactions. The system of 1,1-dimethylhydrazine with its transformation products presenting in the environment has a large negative impact on ecosystems and human health [3]. Therefore the monitoring of contamination of environmental objects by rocket fuel includes one of the important stages – determination of 1,1-dimethylhydrazine.

There are some techniques of determination of 1,1-dimethylhydrazine in environmental objects. Most of them are based on the methods of high performance liquid chromatography and gas chromatography. But they have many disadvantages such as time and labor consuming, expensive sample preparation techniques. For example, the method of liquid chromatography, most commonly used in the analysis of environmental objects for the presence of 1,1-dimethylhydrazine, is based on the alkaline distillation stage, derivatization with n-nitrobenzaldehyde followed by chromatographic analysis. One of the main problems of this method is the formation of 1,1-dimethylhydrazine as the result of reaction of derivatization agent (n-nitrobenzaldehyde) with products of 1,1-dimethylhydrazine transformation presenting in samples, which leads to wrong results of analysis [2]. Determination of 1,1-dimethylhydrazine by gas chromatography is also difficult to perform due to the chemical, and physico-chemical properties of the analyte such as thermal instability, high reactivity and polarity [1].

One of the perspective methods of 1,1-dimethylhydrazine determination to be developed is based on solid phase microextraction (SPME) as a sample preparation stage, separation by gas chromatography with determination of analyte by mass-spectrometry (GC/MS). This method was improved by including derivatization in sample preparation stage. Acetone was proposed as derivatization agent due to its physic-chemical and chromatographic properties [1]. Product of the reaction of 1,1-dimethylhydrazine with acetone – acetone dimethylhyrazone – shows such properties that are suitable for determination of it by GC/MS method. Thus the aim of this work was to study the reaction between 1,1-dimethylhydrazine and acetone, to establish the possibility of using this reaction in determination of 1,1-dimethylhydrazine and to optimize the reaction conditions and SPME parameters for better response of acetone 1,1-dimehtylhydrazone.

Experiments were carried out using the reaction of 1,1-dimethylhydrazine and acetone in vials. Such parameters reaction and SPME as reaction time, reaction temperature, fiber composition, derivatization agent concentration, addition of auxiliary reagents and sample volume were studied, as well as chromatographic parameters. Results of the experiments showed that the optimal time for reaction of 1,1-dimethylhydrazine and acetone is 15 min and temperature of reaction is room temperature. Extraction with polydimethylsiloxane fiber is established to be optimal when it is carried out in 1 min. Different amounts of acetone added to the sample were also studied, and it was established that with the increasing of acetone amount the response of acetone 1,1-dimethylhydrazone increases as well. Sodium chloride, acetic acid and potassium hydroxide addition was also studied. The addition of salt increases the response of analyte in several times. However, this addition has negative impact on calibration curve breaking its linearity. Addition of acid and alkali decrease the response of the analyte, which is not acceptable in determination of 1,1-dimethylhydrazine.

Experiments carried out using acetone as derivatization agent allowed to conclude that this method of 1,1-dimethylhydrazine determination can be very perspective, and development of this method can solve the main problems of the analysis of environmental objects for the presence of such toxic compound.

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