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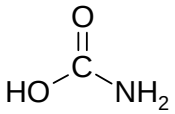
MAN-CAUSED-ECOLOGICAL AND CHEMICAL-TOXICOLOGICAL SAFETY OF UTILIZATION OF THE PESTICIDES ON BASIS OF CARBAMIC ACID DERIVATIVES

The carbaryl (sevine) as high-performance pesticide which is widely used against vermin of agriculture crops and of trees and which influences the chemical-toxicological and the man-caused-ecological safety is considered in this article. The technique of extraction of the carbaryl from bioactive substances is propounded. Furthermore the conditions of the additional purification of the carbaryl from admixtures in the extracts from biological material were hand-picked. The reversed-phase chromatography (RPC) method for qualitative and quantitative determination of the carbaryl extracted from biological material and from air was elaborated.

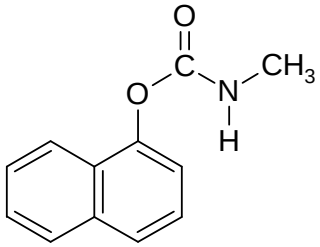
Keywords: carbaryl, extraction, purification, analysis, backward-phase liquid chromatography.

Introduction. The number of the pesticides (these are mainly organic substances) has more than 100,000 names. Toxicological significance of these pesticides consists in its biological activity. They are able to destroy not only harmful insects, weeds etc. they also adversely affect upon the cultivated plants, domestic animals and people. The side effect of wide use of pesticides is reflected also in environmental pollution. Everything without exception pesticides possesses mutagen action or any other negative influence on wildlife and people. About 90% of all fungicides, 60% of herbicides and 30% of insecticides are carcinogens. It is counted the 98% of insecticides do not attain one's object and accumulate in water and in air [1].

The wrong storage, violation of the transportation rules and non-compliance with operational terms are the main reasons of acute poisoning by pesticides. Therefore the technique elaboration of the chemical and toxicological analysis for identification and determination of pesticides in foodstuff, biological materials and biological liquid of organisms possess great significance for the preventive measures of poisonings by pesticides. The carbamic acid derivatives also are these pesticides:



The vast number of carbamic acid ester is synthesized, however among them the greatest application has carbaryl (sevine), named by I.U.P.A.C. system as naphthalen-1-yl methylcarbamate:



They call carbaryl else as arapsine, arylat, vetocs, denapon, carbamate, mervin, naphthylcarbamate, pantrine, preparation 7744, sevine, sevinox, three-carname and others.

The carbaryl is white crystal odourless (melting temperature is 142°C) slightly soluble in water but it well soluble in the majority of organic solvents. It is able to have been remained in the soil about one year. The carbaryl does not decompose almost when heating to 70°C. It easily hydrolyzes in neutral, acid and alkaline solutions. Products of hydrolysis are naphtho-1 and some other metabolites [2].

The carbaryl is produced in the form of the wetting agents (50-85%), dusts and granules. It is used as a highly effective insecticide for combating agricultural pests of crops and trees. The carbaryl after penetrating into a stomach rapidly soaks into blood whereupon it rapidly spreads onto all organs. The liver function as well as a proteinaceous and anti-toxic function collapses by long-term exposure of the carbaryl onto an organism. Eyes, skin, respiratory tract become irritated after short-term influence of the carbaryl. The carbaryl penetrates in an organism through skin and a mouth after aerosol inhalation. Thus there comes dizziness, spasms, heavy breath, nausea, consciousness loss *etc*. The maximum concentration limit of the carbaryl in air of a working area is 1 mg/m^3 [2].

In addition the carbaryl is combustible substance. The flash point, ignition and autoignition temperatures are 169, 196 and 560°C respectively; the nether concentration limit of flame spreading, the maximum explosion pressure and minimum ignition energy equal to 15 g/m^3, 620 kPa and 10 mJ respectively. Burning of the carbaryl is accompanied by formation of toxic vapours of nitrogen oxides. It also reacts with strong oxidizers, predetermining thus possibility of a conflagration and explosion.

Analysis of early researches and publications. From references [1, 3-5] it is known that for identification of the carbaryl are used the microcrystal and microscopical reactions with picric acid and mercury(II) chloride, the recrystallization reactions from alcoholic or chloroformic solution, the colour reaction with 4-aminoantipyrine, with a mix of copper(II) chloride and sodium bromide as well as the chromatography method in a thin layer of a sorbent [2].

The previous researchers elaborated a photocolorimetric method of quantitative determination of the carbaryl based on alkaline hydrolysis of the chemical. Thus the metabolite like 1-naphthol is formed. It convert into the painted in blue colour compound by means of diazotized *para*-nitroaniline [2].

The qualitative and quantitative analysis of the carbaryl realize in a biological material after extraction by benzene and processing of the obtained residue by a phosphate-acetone mixture with the follow-up purification [1]. Among modern methods of the quantitative analysis a method of a high-performance liquid chromatography (HPLC) is described in [6].

Many scientific publications are consecrated to chemistry of pesticides. At the same time of the works, consecrated to the chemical toxicological analysis of pesticides in such sophisticated objects as internal, blood, urine is a little. Therefore, a choice of methods of isolation, of purification, of qualitative and quantitative determination of organic pesticides is an important scientific and technical issue.

The work purpose were to elaborate the techniques of isolation, purification, qualitative and quantitative determination of the carbaryl extracted both from a biological material and from air using the method of the reversed-phase chromatography for liquid.

Experimental results and their discussion. *The isolation and purification of the carbaryl.* The carbaryl has been extracted out of the crushed biomaterial (100 g) by N-hexane (three extractions on 100 ml each). So each extraction proceeded about 1 hour. All hexanoic extractions unite whereupon centrifugalize approximately 5 minutes (10 000 rpm). Centrifugate is evaporated until dry at the room temperature. The dry residuum has been dissolved in 10 ml of ethanol. If colour of the obtained solution was brown, then that was purified extra by means of addition of 15 % solution of ammonium chloride. The final solution was filtered out whereupon a filtrate was frozen out in the freezer of 30 min. A diethyl ether (20 mL) was added to the obtained sample and it was twice extracted by ether (on 20 ml each). Note that 1-naphtho (a hydrolysis product) can pass on from a biomaterial to an etheric layer; that is a hindrance for identification of the carbaryl. For separation of the carbaryl and naphtol the 2% solution of sodium hydroxide (20 ml) was added to the united etheric extraction and it all was shaken up in the separating funnel. After formation of two liquid layers the aqueous portion separates off the etheric one. The ether from the etheric extraction was evaporated. The dry residuum was dissolved in 5 ml of ethanol and this solu-

tion was examined for the presence of the carbaryl (the aqueous phase was examined for the presence of the 1-naphtho). This was done by using the qualitative reactions described in references [2, 6] as well as by means of proposed by us of the reversed-phase chromatography (RPC) technique.

Determination of the carbaryl by reversed-phase chromatography (RPC). The extracted from biomaterial and purified the prototype of the carbaryl (10 ml) was put into chromatograph of the *Cvet-304* model with ultra-violet detector (254 nm) and chromatographic column made of stainless steel (10?0.4 cm). The sorbent is a silica gel C-3 (S = 260 m^2/g) with modified by *n*-alkyl chains C_{16} (particle size of a silica gel are 10 μm). The eluent is a mix of the isopropyl alcohol and water (at a ratio of 35 to 65) with added 0.25 % ammonia aqueous solution. The elution rate, pressure and thermostat temperature are 1 cm^3/min, 40 bar and 50°C respectively.

Under these conditions of chromatography the retention time of the carbaryl equals 5 min. and 10 sec. The result was averaged on five measured values. The quantitative contents of the carbaryl are determined by a method of absolute calibration. For this purpose the solution of the carbaryl in ethyl alcohol with mass concentration of 0,0636% was prepared. This solution was put into the chromatograph in quantity 0,6, 1,0 and 1,6 μl. For them the chromatogram was written down. The retention time and peak height were recorded.

The actual content of the carbaryl in investigated sample are given in Table. The linear dependence was graphed in coordinates: peak height – substance content in sample (Fig.). These data show that in the range of the specified concentration the rectilinear dependence between peak height and a mass portion of the carbaryl is well-defined.

Table 1

The content of the carbaryl in investigated sample

Studied substance	Retention time, min	Initial mass concentration, %	Mass concentration of the diluted solutions, %	The taken sample, μl	Quantity of substance in the taken volume, mg	Peak height, mm
Carbaryl	5,17	0,0636	0,0190 0,0318 0,0509	0,6 1,0 1,6	$0{,}284\cdot10^{-3}$ $0{,}474\cdot10^{-3}$ $0{,}758\cdot10^{-3}$	78 120 181

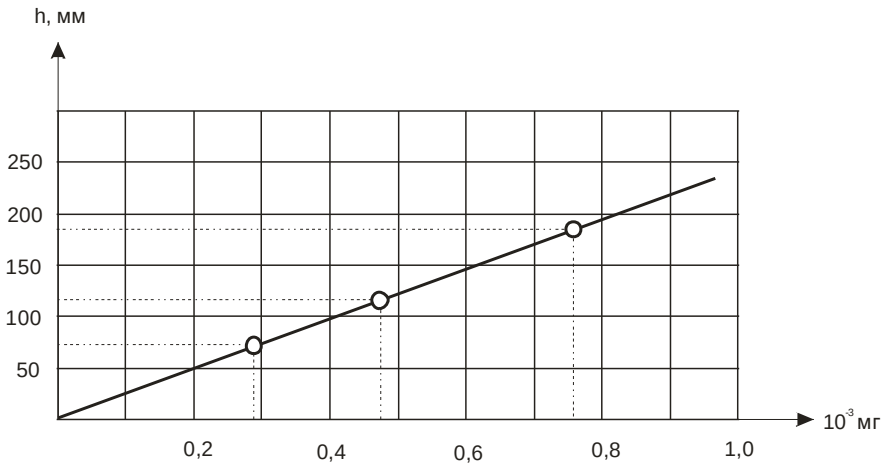


Fig. 1. *Plot of the content of substance in test versus peak height (h)*

Qualitative and quantitative determination of the 1-naphtho. Alkaline solution which remained after extraction of the carbaryl by ether was neutralized by solution of the hydrochloric acid and 1-naphtho was extracted by chloroform (three times on 15 ml). The collected together the chloroformic extracts were evaporated on dryly and the residue was dissolved in 5 ml of ethanol. This solution is used for the qualitative analysis of 1-naphtho on reaction with a mix of copper(II) chlo-

ride and sodium bromide (red-blue or blue-violet colour), with sodium nitrite in sulphuric acid (yellow colour which after alkalifying of the solution becomes canary colour), with solution of ferrous(III) chloride (pink-violet colour) [1].

Determination of the carbaryl in air. Air (50 L) (volumetric rate is 10 L/min) was passed through the filter (AFA – VP – 10). This filter was first steeped into the ethanol, then was squeezed out and again twice was washed out by the ethanol. The ethanolic extracts were collected together and were evaporated. The obtained residue was dissolved in 1 ml of the ethanol and was studied for the purpose of presence of the carbaryl using qualitative reactions and a method of reversed-phase chromatography for liquids.

Conclusions. The reversed-phase chromatography (RPC) method for isolation and purification of the carbaryl extracted from biological material was elaborated. The scopes of application of the elaborated technique of qualitative and quantitative determination of the carboryl in a biological material and air were pointed

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ТЕХНОГЕННО-ЕКОЛОГИЧЕСКАЯ И ХИМИКО-ТОКСИКОЛОГИЧЕСКАЯ ОПАСНОСТЬ ИСПОЛЬЗОВАНИЯ ПЕСТИЦИДОВ НА ОСНОВЕ ПРОИЗВОДНЫХ КАРБАМИНОВОЙ КИСЛОТЫ

Карбарил (севин) – производное вещество карбаминовой кислоты, используется в качестве высокоэффективного инсектицида для борьбы с вредителями сельскохозяйственных культур и деревьев. Нами предложена методика выделения карбарила из биологического материала, а также подобраны условия дополнительной очистки карбарила от примесей биологического происхождения, которые находятся в вытяжках из биологического материала. Разработан высокочувствительный, репродуктивный метод качественного и количественного анализа карбарила, выделенного из биологического материала, и в воздухе обратно - фазовой хроматографией.

Ключевые слова: карбарил, выделение, очистка, анализ, обратно - фазовая жидкостная хроматография.

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ТЕХНОГЕННО-ЕКОЛОГІЧНА ТА ХІМІКО-ТОКСИКОЛОГІЧНА БЕЗПЕКА ВИКОРИСТАННЯ ПЕСТИЦИДІВ НА ОСНОВІ ПОХІДНИХ КАРБАМІНОВОЇ КИСЛОТИ

Карбарил (севін) – похідне карбамінової кислоти, використовується як високоефективний інсектицид для боротьби з шкідниками сільськогосподарських культур і дерев. Нами запропоновано методику виділення карбарилу з біологічного матеріалу, а також підібрано умови додаткової очистки карбарилу від домішок, які знаходяться в витяжках з біологічного матеріалу. Розроблено високочутливий метод якісного і кількісного аналізу карбарилу, виділеного з біологічного матеріалу і в повітрі обернено – фазовою рідинною хроматографією.

Ключові слова: карбарил, виділення, очистка, аналіз, обернено – фазова рідинна хроматографія

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