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METHOD OF CONTROLLING HEALTH SAFE LEVELS OF DIMETHYL DICARBONATE CONTENT (DMDK, E-242) IN THE AIR OF THE WORKING AREA

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ABSTRACT. *Existing in Ukraine sanitary legislation on the introduction of chemicals into the national economy provides for compliance with regulations. Since the control over the presence of DMDK in the air of the working area is carried out only with the help of indicator paper, there was a need to develop a gas chromatographic method for its determination in the air of the working area by modeling the conditions of industrial use of the drug.*

Aim of the Research. *To analyze research from available sources of information on the peculiarities of the use of dimethyldicarbonate (E 242, Velcorin), as well as regulations for its use and control.*

Materials and Methods. *Review and analysis of scientific publications, directives and regulations of the EU. Gas chromatography method. Materials: silochrome C-120, fraction 0,35-0,5 mm according to TU 6-09-17-48; KSK brand silica gel according to GOST 3956; glass wool according to the current ND; DMDK, analytical standard, 99,9%, CAS 4525-33-1; acetonitrile, Sigma-Aldrich No 34851. Computer data processing system and metrological evaluation of the methodology.*

Results and Discussion. *The conducted research allowed to offer a modern method of determining the levels of DMDK in the air of the working area by concentrating it and detecting it by gas chromatography.*

The developed method allows to control compliance with the levels of DMDK content in the air of the working area in accordance with the requirements of GOST 12.1.016-79 "Air in the working area. Requirements for methods for measuring concentrations of harmful substances" at the level of j the value of the hygienic standard.

Conclusions. *The proposed method of measuring the mass concentrations of DMDK is based on the use of gas chromatography using a flame ionization detector (FID). It allows to determine Velcorin in the range of mass concentrations from 0,1 to 0,5 mg/m^3, the lower limit of its quantitative determination makes 0,1 mg/m^3 at selection of 5 m^3 of air.*

The relative standard deviation when using this method is 1,41%, the confidence limits of the random error – 0,04%, the total error of the measurement result – 12,24%, not exceeding + 25% and meeting the requirements of GOST 17.2.3.01-86.

Keywords: *dimethyldicarbonate, E 242, Velcorin, air of the working area, gas chromatography method, indicator paper, ASLE, silochrome, flame ionization detector, sorption tubes, acetonitrile, chromatograms, metrological evaluation, concentration, detection.*

Introduction. Solving this problem, the features of the DMDK should be taken into account, in particular, its physicochemical properties: rapid destruction in the presence of water molecules with the formation of methyl alcohol and carbon dioxide. The relevance of this research is due to the need to introduce into the technological processes of production of wines, juices and soft drinks in Ukraine modern, widespread in the European Union and many countries of the world preservative dimethyldicarbonate (DKDM, E242, Velcorin). According to the current legislation the obligatory condition is existence of hygienic regulations of safe use of this substance, including its maximum admissible concentration in air of a working zone, as well as a chemical-analytical method for control.

Aim of the Research. To analyze the data of domestic and foreign literature on modern technological processes of using DKDM, physical and chemical properties, regulations of its application. Based on the obtained data to scientifically substantiate the method of chemical-analytical control over the levels of the substance in the air of the working area.

Material and Methods. Review and analysis of scientific publications, directives and regulations of the EU. Gas chromatography method. Materials: silochrome C-120, fraction 0,35-0,5 mm according to TU 6-09-17-48; KSK brand silica gel according to GOST 3956; glass wool according to the current ND; DMDK, analytical standard, 99,9%, CAS 4525-33-1; acetonitrile, Sigma-Aldrich No 34851. Computer data processing system and metrological evaluation of the methodology.

Results and Discussion. The peculiarity of dimethyldicarbonate is its low stability. It is destroyed in the process of making drinks, does not affect their taste and color and in its native form does not enter the human body. During the decomposition of dimethyldicarbonate, methanol is formed, its amount is insignificant (from 250 mg of dimethyldicarbonate – 120 mg of methanol and 164 mg of CO_2).

According to the Council of Europe Directive 95/2/EC of February 20, 1995 [2] dimethyldicarbonate (E-242) is used for cold sterilization of soft drinks, wines, soft wines, cold teas in a concentration of not more than 250 mg per liter of beverage.

The Resolution of the Chief State Sanitary Doctor of Ukraine of January 28, 2002 has been in force in Ukraine since 2002 No 3 "On approval of the values of hygienic standards of food additive dimethyldicarbonate E 242 in food products" [3], which approved the maximum permissible level of food additive dimethyldicarbonate E 242 in soft drinks not more than 250 mg / l recommended by the Committee for Hygienic Regulation of the Ministry of Health of Ukraine.

According to the latest documents adopted in the EU, the scope of dimethyldicarbonate has been expanded. Thus, Regulations (EU) No 1333/2008 of the European Parliament and of the Council of December 16, 2008 on food additives [4], No 1129/2011 of the European Parliament and of the Council of November 11, 2011 amending Annex II to Regulation (EU) 1333/2008 by establishing a consolidated list of food additives [5], No 1166/2012 of the European Parliament and of the Council of December 7, 2012 [6], which provides for amendments to Annex II to Regulation (EU) 1333/2008, Velcorin is authorized for use in non-alcoholic flavored beverages, non-alcoholic wines, liquid tea concentrates, cider and pear cider, low-alcohol wines, fruit and berry wines, products based on wines covered by Regulation (EU) No 1601/91 [7], other alcoholic beverages, including mixtures of alcoholic beverages with non-alcoholic and wine alcohols containing less than 15% alcohol. The maximum permitted level is left unchanged – 250 mg of dimethyldicarbonate per liter of drink, in grape and honey wine – 200 mg per liter of drink.

In order to control the observance of the specified hygienic standard, the Center for Product Quality Control of the Ukrainian Research Institute of Alcohol and Food Biotechnology and CJSC "National Analytical Center" was developed and certified in accordance with the requirements of GOST 8.010-99 "Methods of measuring the content of methanol in beverages after preservation with dimethyldicarbonate (E 242) by gas chromatography" (MVV 081/12-0320-06) [8].

According to the current legislation of Ukraine, the introduction of a new substance in the technological processes of beverage production requires the development and approval in the prescribed manner of its regulations not only in the objects of application, but also in the air of the working area.

Modern technology of use of DMDK practically excludes a possibility of its receipt in air of a working area. But in certain emergencies – depressurization of equipment, violation of the conditions of transportation, storage and disposal of Velcorin – it is possible to contaminate production and storage facilities.

Control over the content in the air of the working area of this preservative in other countries is carried out using indicator paper, which is attached to each of its packaging units. A change in the color of the indicator paper indicates the presence of the substance in the air. Using such an indicator, dimethyldicarbonate in the air of the working area can be detected at a concentration of 0,04 ppm. This level corresponds to the lower limit of sensitivity of this method of indication of the substance.

Taking into account the recommendations of the European Union on the permissible harmless level of DMDK in the air of the working area (0,05 and 0,13 mg/m^3), it was recommended to approve the value of the approximate safe level of exposure (ASLE) at the level of 0,1 mg / m^3 (vapor) with the note "dangerous in contact with skin and eyes".

The current sanitary legislation in Ukraine for the introduction of a chemical substance into the

national economy requires a standard, which was done by modeling the conditions of industrial use of the drug and the development of gas-chromatographic method for its determination in the air of the working area.

The method is intended for laboratory centers and research institutions of the Ministry of Health of Ukraine, veterinary, agrochemical and control toxicological laboratories of the Ministry of Agriculture of Ukraine and laboratories, the scope of which includes determining the levels of DMDK content in the air of the working area.

DMDK is a colorless liquid with a slightly pungent fruity odor. Melting point 17°C; boiling point 172°C (approximately at a temperature of 70°C decomposition begins); density 1,25 g/ml. Storage temperature 20-30°C. Well soluble in alcohol, soluble in water and toluene.

In order to find adequate methods and means of adsorption of DMDK from the air, we conducted a review of the scientific literature, the result of which showed, that recently activated calcined microporous sorbents silochrome S-80 and S-120 are widely used [9]. The main advantages of silochrome are its resistance to mechanical and thermal effects, as well as low intrinsic catalytic activity. The surface of the silochrome is covered with hydroxyl groups, which determines its ability to purposefully modify. Unlike activated carbon, these classes of sorbents actively absorb and give well into the eluate organic matter of certain groups.

The proposed principle of the method of measuring the mass concentrations of DMDK is based on the use of gas chromatography using a flame ionization detector (GC-FID) in the range of mass concentrations from 0,1 to 0,5 mg / m^3 (limit of quantitative determination of 0,1 mg / m^3 with the selection of 5 m^3 of air).

To substantiate the method, we have proposed the following reagents and materials: silochrome C-120, fraction of 0,35-0,5 mm in accordance with TU 6-09-17-48; KSK brand silica gel according to GOST 3956; glass wool according to the current ND; DMDK, analytical standard, 99,9%, CAS 4525-33-1; acetonitrile, Sigma-Aldrich No 34851.

Preparation of the sorbent included washing with several portions of acetonitrile, followed by calcination in an oven at 200°C for 4 hours. After cooling, the finished sorbent was placed in a beaker with a well-ground glass stopper, stored in a washed and thoroughly dried desiccator, at the bottom of which was placed a pre-dried layer of silica gel KSK.

Sorption tubes were prepared immediately before sampling. 0,5 g of S-120 silochrome was placed in each of them, fixed with fiberglass and closed with Teflon caps or a silicone hose with glass plugs. Sampling was performed simultaneously with concentration on the solid sorbent, followed by extraction of DMDK from the sorbent layer with acetonitrile.

Therefore, this method is specific, dimethyl carbonate, diphenyl carbonate and methyl phenyl carbonate do not interfere with the determination. The relevant standard environmental conditions were observed during the measurements.

Preparation of solutions and preparation of the sample for analysis was carried out in microclimatic conditions in accordance with the requirements of SSN 3.3.6.042-99 “Sanitary norms of microclimate of industrial premises”, approved by the resolution No 42 of the Chief State Sanitary Physician of Ukraine dated December 1, 1999 [10], the measurement on the chromatograph was carried out in the conditions recommended by the operating documents for the device.

To control our proposed hygienic standard DMDK at the level of 1/2 ASLE and, based on the sensitivity of the selected detection method (GC-FID), the required volume of air for aspiration, which is 5,0 m^3, was calculated. To select it at the inlet of the aspirator installed cartridges with sorbent. Air with a volume flow rate of 10 dm^3 / min was aspirated through sorption tubes. During sampling, the air temperature, atmospheric pressure, volumetric aspiration rate on the rotameter, and sampling time were recorded. Selected samples were capped and placed in tubes with ground stoppers. Selected samples were analyzed during the day.

Sample preparation and measurements were performed in stages. The glass wool was removed from the sorption tubes, the sorbent was poured into the weighing bottle and filled with acetonitrile. The weighing bottle was placed in an ultrasonic bath and kept for 10 minutes.

Measurements were performed on a gas chromatograph with FID under the following conditions: atmospheric pressure from 84,0 kPa to 106,7 kPa (from 630 mm Hg to 800 mm Hg); relative humidity (at a temperature of 25°C) not more than 85%; indoor air temperature (20 ± 5)°C;

voltage in the electrical supply network of devices (220 ± 20) V; frequency of electric current in the network (50 ± 0,5) Hz; chromatographic column HP-5 30 m, 0,32 mm, 0.25 μm, manufactured by Agilent (or similar); silochrome C-120, fraction of 0,35-0,5 mm in accordance with TU 6-09-17-48; KSK brand silica gel according to GOST 3956; glass wool according to the current ND; DMDK, analytical standard, 99,9%, CAS 4525-33-1; acetonitrile, Sigma-Aldrich No 34851.

The obtained chromatograms recorded the peaks in the time of DMDK retention and determined their areas using a computer data processing system. The average value of the DMDK peak area for each of the parallel samples was calculated.

Using the calibration dependence, the results of measurements and calculations of the areas of the chromatographic peaks of DMDK in the samples, calculated the mass concentration of DMDK in the air of the working area (mg/m^3) for each of the parallel samples.

After completion of researches and reception of positive results the metrological assessment of a technique according to GOST 12.1.016-79 was carried out. "Air in the working area. Requirements for methods for measuring concentrations of harmful substances" [11]. According to these calculations, it was found that:

– the relative standard deviation is 1,41%;

– confidence limits of random error – 0,04%;

– the total error of the measurement result is 12,24%, which does not exceed + 25% and meets the requirements of GOST 17.2.3.01-86 [11].

Thus, the conducted research allowed to offer a modern method for determining the levels of DMDK in the air of the working area by concentrating it on silochrome C-120 and detection by gas chromatography with FID. The developed method allows to carry out control over observance of the hygienic standard (ASLE) DMDK in air of a working zone according to requirements of GOST 12.1.016-79 "Air in the working area. Requirements for methods for measuring concentrations of harmful substances" at the level of j the value of the hygienic standard [12].

Conclusions. The proposed method of measuring the mass concentrations of DMDK can be based on the use of gas chromatography using a flame ionization detector (FID). It allows to determine Velcorin in the range of mass concentrations from 0,1 to 0,5 mg/m^3, the lower limit of its quantitative determination makes 0,1 mg/m^3 at selection of 5 m^3 of air. The relative standard deviation when using this method is 1,41%, the confidence limits of random error – 0,04%, the total error of the measurement result is 12,24%, which does not exceed + 25% and meets the requirements of GOST 17.2.3.01-86.

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МЕТОД КОНТРОЛЮ ЗА БЕЗПЕЧНИМИ ДЛЯ ЗДОРОВ’Я РІВНЯМИ ВМІСТУ ДИМЕТИЛДИКАРБОНАТУ (ДМДК, Е-242) У ПОВІТРІ РОБОЧОЇ ЗОНИ

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РЕЗЮМЕ. *Існуюче в Україні санітарне законодавство щодо впровадження хімічної речовини в народне господарство передбачає відповідність нормативних документів. Оскільки контроль за наявністю ДМДК у повітрі робочої зони здійснюється лише за допомогою індикаторного паперу, виникла необхідність розробки газохроматографічного методу його визначення в повітрі робочої зони шляхом моделювання умов промислового використання препарату.*
Мета роботи. *Провести аналіз досліджень із доступних джерел інформації про особливості використання диметилдикарбонату (Е 242, велькорину), а також регламенти його застосування та можливості контролю.*
Матеріали та методи. *Огляд та аналіз наукових публікацій, директив та регламентів ЄС. Метод газової хроматографії. Матеріали: силохром С-120, фракція 0,35-0,5 мм згідно з ТУ 6-09-17-48; силікагель марки КСК згідно з ГОСТ 3956; скловата згідно з чинною НД; ДМДК, аналітичний стандарт, 99,9 %, CAS 4525-33-1; ацетонітрил, фірма Sigma-Aldrich №34851. Компьютерна система обробки даних та метрологічна оцінка методики.*
Результати*. Проведені дослідження дозволили запропонувати сучасний метод визначення рівнів вмісту ДМДК у повітрі робочої зони шляхом його концентрування та детектування методом газової хроматографії.*
Розроблений метод дозволяє здійснювати контроль за дотриманням рівнів вмісту ДМДК у повітрі робочої зони відповідно до вимог ГОСТ 12.1.016-79 “Воздух рабочей зоны. Требования к методикам измерения концентраций вредных веществ” на рівні ј величини гігієнічного нормативу.
Висновки. *Запропонований метод вимірювання масових концентрацій ДМДК ґрунтується на використанні газової хроматографії з застосуванням полум'яно-іонізаційного детектора (ПІД). Він дозволяє визначити велькорин у діапазоні масових концентрацій від 0,1 до 0,5 мг/м^3, нижня межа його кількісного визначення становить 0,1 мг/м^3 при відборі 5 м^3 повітря.*
Відносне середнє квадратичне відхилення при використанні даного методу становить 1,41 %, довірчі межі випадкової похибки – 0,04 %, сумарна похибка результату вимірювань – 12,24 %, що не перевищує 1/4 25 % і відповідає вимогам ГОСТ 17.2.3.01-86 .
Ключові слова: *диметилдикарбонат, Е 242, велькорин, повітря робочої зони, метод газової хроматографії, індикаторний папір, ОБРВ, силохром, полуменево-іонізаційний детектор, сорбційні трубки, ацетонітрил, хроматограми, метрологічна оцінка, концентрування, детектування.*

МЕТОД КОНТРОЛЯ ЗА БЕЗОПАСНЫМИ ДЛЯ ЗДОРОВЬЯ УРОВНЯМИ СОДЕРЖАНИЯ ДИМЕТИЛДИКАРБОНАТА (ДМДК, Е-242) В ВОЗДУХЕ РАБОЧЕЙ ЗОНЫ

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РЕЗЮМЕ*. Существующее в Украине санитарное законодательство по внедрению химического вещества в народное хозяйство предполагает наличие соответствующих нормативных документов. Поскольку контроль за наличием ДМДК в воздухе рабочей зоны осуществляется только с помощью индикаторной бумаги, возникла необходимость разработки газохроматографического метода его определения в воздухе рабочей зоны путем моделирования условий промышленного применения препарата.*

Цель работы. *Провести анализ исследований из доступных источников информации об особенностях использования диметилдикарбоната (Е 242, велькорину), а также регламенты его применения и возможности контроля.*

Материалы и методи. *Обзор и анализ научных публикаций: силохром С-120, фракция 0,35-0,5 мм согласно ТУ 6-09-17-48; силикагель марки КСК согласно ГОСТ 3956; скловата согласно с действующей НД; ДМДК, аналитический стандарт, 99,9 %, CAS 4525-33-1; ацетонитрил, фирма Sigma-Aldrich №34851. Компьютерная система обработки данных и метрологическая оценка методики.*

Результаты. *Проведенные исследования позволили предложить современный метод определения уровней содержания ДМДК в воздухе рабочей зоны путем его концентрирования и детектирования методом газовой хроматографии. Разработанный метод позволяет осуществлять контроль за соблюдением уровней содержания ДМДК в воздухе рабочей зоны в соответствии с требованиями ГОСТ 12.1.016-79 "Воздух рабочей зоны. Требования к методикам измерения концентраций вредных веществ "на уровне j величины гигиенического норматива.*

Выводы. *Предложенный метод измерения массовых концентраций ДМДК основывается на использовании газовой хроматографии с применением пламенно-ионизационного детектора (ПИД). Он позволяет определить велькорин в диапазоне массовых концентраций от 0,1 до 0,5 мг/м^3, нижняя граница его количественного определения составляет 0,1 мг/м^3 при отборе 5 м^3 воздуха. Относительное среднее квадратическое отклонение при использовании данного метода составляет 1,41%, доверительные границы случайной погрешности – 0,04 %, суммарная погрешность результата измерений – 12,24 %, что не превышает 25 % и соответствует требованиям ГОСТ 17.2.3.01-86.*

Ключевые слова: *диметилдикарбонат, Е 242, велькорин, воздух рабочей зоны, метод газовой хроматографии, индикаторная бумага, ОБУВ, силохром, пламенно-ионизационный детектор, сорбционные трубки, ацетонитрил, хроматограммы, метрологическая оценка, концентрирование, детектирование.*

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