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PECULIARITIES OF MULTIDISCIPLINARY FORENSIC RESEARCH ON HYDROLYSIS LIGIN

The article deals with the peculiarities of complex expert research of lignin, since knowledge of the forensic and chemical and forensic examinations was required. It was noted that in the microscopic study, all of the samples submitted for research revealed small particles of brown wood with different shades and brown conglomerates. The maceration method investigated specially processed samples of the substances provided. A qualitative reaction to lignin revealed the presence of molecules provided for the study of substances, the conifer aldehyde group and the structural chain that is characteristic of lignin. Qualitative reactions revealed that iron, calcium, magnesium, aluminum and sulfate ions were identified in all lignin samples, which characterizing qualitative composition of vegetable raw materials. It has been determined that further studies of lignin should be carried out in a well-established manner, namely: determination of carbon content; quantitative determination of solids and hygroscopic moisture; determination of ash content; determination of the quantitative content of calcium; quantitative determination of magnesium; determination of quantitative content of iron.

Keywords: lignin, microscopic investigations, qualitative reactions, properties, content of substances.

Formulation of Research Problem. The issue of environmental quality assurance in Ukraine is related to the reduction of environmental burden of waste of various origins. The problem of industrial waste disposal is caused by the reduction of some types of resources and the possibility of manufacturing recyclable products with lower production costs and high quality of the final product. The economic and technical nature of waste management is closely linked to several measures to protect the environment and use natural resources[1].

[1] *Shmandyi V. M., Pliatsuk D. L.* Peredumovy pobudovy modeli imovirnisnoho rozpodilu zabrudniuiuchykh rechovyn v atmosferi [Prerequisites for constructing a model of probable distribution of pollutants in the atmosphere]. Naukovyi zhurnal «Ekolohichna bezpeka». Kremenchuk : KrNU. 2014. № 2 (18).

Hydrolysis plants can be considered as waste-producing enterprises. The hydrolysis plants mainly process sawmill and woodworking waste: sawdust, crushed sawmill waste (slopes, rails) and wood for obtaining, among other things, a commodity product such as hydrolysis lignin. In the technologies of production of lignin based on waste of vegetable raw materials use various methods that affect its properties.

Analysis of Current Researches and Publications.

In the processing of vegetable raw materials by a complex method is complete hydrolysis of polysaccharides, and lignin remains in the form of insoluble residue, the humidity of which is 20%. In the complex processing of coniferous wood for cellulose and other products, when only hydrolysis of hemicellulose polysaccharides is provided, water-soluble lignin is formed. Technical or hydrolytic lignin after hydrolysis with dilute acids remains insoluble in water, but a small number of active groups are formed, which form methyl alcohol, formaldehyde, acetic acid and formic acid. In the waste of this production, in addition to hydrolysis of lignin, there are residues of plant tissue[1].

Problems of the use of wood waste are also considered in the scientific works of other scientists, among them: M. S. Gabrel, G. G. Geletukha, T. A. Zhelezna, M. M Zhovnir, A. M. Deineka, P. R Puzentilo, M. B. Svintukh and others. However, the papers of these authors did not pay attention to complex expert study of lignin.

The **Article Purpose** is to outline the features of a comprehensive expert study of lignin.

Main content presentation. Despite the development of processing technologies, the issue of the generation of waste that is harmful to the environment remains open. Along with the problem of environmental pollution is the problem of illegal production of lignin hydrolysis brand L-4 to sell it at the consumer market at inflated prices. That is why environmentalists and law enforcement officials initiated criminal proceedings and prepared a motion to appoint a forensic examination of materials, substances and articles. Knowledge in the fields of forensic-chemical and forensic-biological expertise was required to resolve the issues raised by the investigators in the forensic examination, therefore, a comprehensive forensic examination was conducted to

S. 56–60. *Povzun O. I., Podkopaiev S. V., Virych S. O., Horiacheva T. V., Dorokh S. H.* Utylizatsiia polimernoho ta lisokhimichnoho vyrobnytstva u dorozhnomu budivnytstvi [Utilization of polymer and forestry production in road construction]. Ekolohichna bezpeka. № 2/2016(22). S. 102–111 [in Ukrainian].

[1] *Basiuk B. I., Obodovych O. M., Lunina A. O.* Analiz metodiv pererobky vidkhodiv roslynnoi syrovyny v tekhnolohiiakh vyrobnytstva hidroliznoho spyrtu, furfurolu ta lihninu [Analysis of methods of processing waste of vegetable raw materials in technologies of production of hydrolysis alcohol, furfural and lignin]. Prom. teplotekhnyka. 2007. T. 29. № 6. S. 33–45 [in Ukrainian].

investigate the substances of chemical industries and specialty chemicals and objects of plant origin. In the expert examination of the samples provided, namely microscopic examination, we used the technique of investigation of objects of plant origin using a stereo microscope MBS-9 (reflected light, magnification 48x) and microscope «Amplival« (transmitted light, magnification 210x, medium – glycerol). When examined in the field of view of the stereo microscope IBS-2 as a part of all samples submitted for the study revealed insignificant particle sizes of brown wood with different shades and conglomerates of brown color.

Maceration in the field of view of the microscope «Ampival« investigated specially processed samples of the given substances. The test specimens of the test substances were treated with concentrated nitric acid, washed twice with distilled water, and then the preparations were prepared in glycerol. At microscopic examination of the prepared preparations it found that macerated particles of each of the substances presented for research contain:

– remains of plant objects in the form of fragments of vessels with numerous pores, which is characteristic of deciduous trees of trees;

– remnants of mechanical tissues, tracheids with large framed pores, arranged in a single row, which is characteristic of coniferous trees;

– other parts of plant origin.

After conducting the microscopic examination, considering the data given in the decision of the initiator of the examination and the results of the external examination, the experts assumed that the substances provided for the study were lignin. To confirm this assumption, a qualitative reaction to lignin was performed. Parts of the substances presented for study separately from each package (6 packages in total) were impregnated with 12% hydrochloric acid solution.

Excess acid was selected by filter paper. The residues prepared in this way were separately applied dropwise with a 5% ethanol solution of phloroglucine, after which the particles of the substance from each package were colored purple-red. Thus, a qualitative chemical reaction established the presence of molecules provided for the study of substances, coniferaldehyde group and the structural chain that is characteristic of lignin. Based on the information obtained, it is concluded that the substances provided for research are the product of synthesis of terrestrial parts of plants: lignin.

Subsequently, the fractional composition of the presented lignin samples was determined using the sieving method using a laboratory sieve set. The results of the study made it possible to establish that the smallest particle size from 0, 5 to 1, 0 mm (9, 3… 12, 5%) was given for the study, and the largest particle size from 1, 0 to 5, 0 mm.

To establish the qualitative elemental composition of the lignins provided for the study, their parts were separately placed in porcelain crucibles, 2 cm^3 of concentrated sulfuric acid was added, heated in a water bath, and 2 cm^3 of distilled water was added. The resulting mixtures were

thoroughly mixed and separately filtered through paper filters into conical flasks. Each crucible and filter were washed 3 cm^3, attaching the wash water to each of the filtrates, respectively. Each of the filtrates was divided into several parts, with which the characteristic qualitative chemical reactions were carried out:

– addition of ammonia solution and sulfosalicylic acid solution in all 6 mixtures obtained revealed ions of iron (appeared brown-red color) in the composition of the lignins provided for research;

– the addition of solutions of ammonia, ammonium chloride and ammonium oxalate in all 6 mixtures obtained revealed calcium ions, as after the addition of solutions initially appeared a white opacity, which gradually turned into a white fine crystalline precipitate, which did not dissolve when added concentrated acid, but readily soluble by the addition of nitric acid;

– addition of solutions of ammonium chloride, sodium phosphate, ammonia in all 6 mixtures obtained revealed magnesium ions, as evidenced by the appearance of a cloudy white color, which gradually turned into a white finely crystalline precipitate, which dissolves with the addition of acetic acid;

– successively added an excess of 20% sodium hydroxide solution and ammonium chloride powder; the resulting mixtures were heated to boiling, followed by the formation of a gelatinous precipitate of white color, which dissolves in excess of solutions of mineral acids; this qualitative chemical reaction proves the presence in the samples of lignin of aluminum ions;

– addition of a solution of hydrochloric acid and 5% solution of barium chloride in all 6 mixtures obtained revealed sulfate ions, because after the addition of solutions initially appeared a cloud of white, which gradually turned into a white precipitate, which is insoluble in mineral acids.

Thus, by qualitative chemical reactions, it was found that iron, calcium, magnesium, aluminum and sulfate ions, which are characteristic of the qualitative composition of the plant material, were detected in all lignin samples tested.

The following studies were conducted in a clearly defined order, namely:

– determination of carbon content;

– determination of the quantitative content of dry matter and hygroscopic moisture;

– determination of ash content;

– determination of the quantitative content of calcium;

– determination of the quantitative content of magnesium;

– determination of the quantitative content of iron.

The quantitative carbon content was determined in fractions less than 0, 25 mm (three samples per object) of all lignin samples submitted for study. At analytical scales, samples of 0,005 g of the indicated

fractions of all lignin samples submitted for the study were taken and placed in conical flasks with a capacity of 100 cm^3, 15,0 cm^3 of 0, 1 N potassium hydroxide solution were poured. The extraction was carried out for 1 hour in an oven at $+165^0$C. After cooling, 1 cm3 of 1% phenylanthranilic acid solution was added to each mixture and titrated with a 0, 2 N solution of Mor salt. The results of the study showed that the carbon content of the samples submitted for study ranges from 57, 0% to 60, 6%.

The amount of hygroscopic moisture and dry matter was determined after drying at 105 ° C to a constant weight of 1, 000 g of each of the given lignin samples. Because of the study it was found that the content of hygroscopic moisture in the samples ranges from 45, 36% to 55, 45%, and the dry matter – from 44, 55% to 54, 64%.

Determination of ash was performed after drying lignin samples, when air-dry samples (1, 000 g) in ceramic crucibles were placed in a muffle furnace and kept at 750 ° C for 2 hours. The ash content of the samples submitted for study ranges from 6, 83% to 13, 78%.

Calcium, magnesium and iron were determined in lignin fractions less than 0, 25 mm (three samples from each object). After determining the ash content, the lignin contents were quantitatively transferred into conical flasks, filled with 10 cm3 with 10% hydrochloric acid, and brought to boiling point. After cooling, the mixture was filtered into 25 cm3 volumetric flasks, the filter and the precipitate were washed with distilled water and added to the resulting filtrates. After such preparation, the samples were used to determine the quantitative content of calcium, magnesium and iron.

To determine the quantitative calcium content of each volumetric flask, using a Mora pipette, 10 cm^3 of hydrochloric acid solution was taken, which was transferred to a glass beaker, 1-2 drops of methyl-mouth indicator were added, and then 10% aqueous ammonia solution was added dropwise to change the color indicator. The cups were then heated on an electric tile until the first bubble appeared. The mixtures were filtered into conical flasks, the beaker and filter washed several times with distilled water to a volume of 150 cm^3 of filtrate. To the resulting filtrate, 5 cm^3 of 20% sodium hydroxide solution, 1 cm3 of 1% sodium sulfide solution and 5% hydroxyl amine hydrochloric acid solution were added to each flask, after which the indicator – dry chromogen dark blue was added. The resulting mixtures were titrated with a 0.02 M complex-III solution and the calcium content was calculated on a dry sample. The calculations showed that the calcium content of the lignin samples provided for the study is from 1, 53% to 1, 83%.

To determine the magnesium content of each of the flasks, which was determined by the quantitative calcium content, was placed a fragment of Congo paper, was added dropwise 10% hydrochloric acid solution to change the color of the paper from red to blue. After that, the mixture was heated until condensate vapor flasks appeared on the walls, a

10% ammonia solution was added dropwise until red Congo paper appeared, and then a chloride-ammonia buffer solution with pH = 10 to 20 cm^3. The mixture is titrated with Complexon-III after the addition of the black chromogen indicator and the magnesium content is calculated. The calculations show that the magnesium content of the lignin samples provided for the study ranges from 0,21% to 0,28%.

To determine the quantitative content of iron from a volumetric flask using a pipette Mora was selected 10 cm3 hydrochloric acid solution and placed in a glass beaker, added dropwise 10% ammonia solution to the appearance of precipitates of one and a half oxides and added 5 cm3 of 1 N hydrochloric acid solution. The mixture was heated to a temperature of + 60… 70 ^{0}C, an indicator of 1 cm^3 solution of 1% sulfosalicylic acid was added, titrated in a hot state with a 0.02 M complex-III solution and the iron content was calculated. The calculations prove that the magnesium content of the lignin samples provided for the study is from 1, 2% to 1, 9%.

Conclusions. According to the results of the conducted researches it is established that the substances submitted for research coincide with each other in appearance, which is confirmed by microscopic examination. The samples also have the same content of iron, calcium, magnesium, aluminum and sulfate ions in their composition. The listed overlapping features are generic in forensic significance, and lignin specimens submitted for research have a common generic identity. However, at the same time, these samples differ in quantitative content of dry matter and hygroscopic moisture, ash content, quantitative content of carbon, iron, magnesium, calcium. Such differences can be explained by different sources of origin of lignins provided for research, as well as technological features of their production, storage conditions, etc. Considering the above, it is not possible to resolve the question of establishing common (different) group membership of the samples submitted for research and whether they were previously a single mass.

Based on the data obtained, it can also be concluded that the characteristics of lignin samples are in accordance with the specifications in the technical documentation for the product[1], namely: the quantitative content of carbon, calcium, magnesium, iron, ash, hygroscopic moisture, dry matter, but submitted for research the samples do not correspond to the quantitative content of the particles, the sizes: less than 0,25 mm; from 0, 25 to 0.50 mm; from 0, 5 to 1,0 mm.

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ОСОБЛИВОСТІ КОМПЛЕКСНОГО ЕКСПЕРТНОГО ДОСЛІДЖЕННЯ ГІДРОЛИЗНОГО ЛІГНІНУ

У статті розглянуто питання щодо особливостей комплексного експертного дослідження лігніну. При мікроскопічному вивченні у складі усіх наданих на дослідження зразках виявлено незначні за розмірами частки деревини коричневого кольору з різними відтінками та конгломератики коричневого кольору. Крім того, мацеровані частки кожної із наданих на дослідження речовин містять залишки рослинних об’єктів. Якісною реакцією на лігнін встановлено наявність у складі молекул, наданих на дослідження речовин, коніферилальдегідної групи та структурного ланцюга, що є характерним для лігніну. Проведеними якісними хімічними реакціями встановлено, що у всіх наданих на дослідження зразках лігніну виявлено іони заліза, кальцію, магнію, алюмінію та сульфат-іони, що є характерним для

якісного складу рослинної сировини. Доведено, що подальші дослідження лігніну мають проводитись у чітко визначеному порядку, а саме: визначення кількісного вмісту вуглецю; визначення кількісного вмісту сухої речовини та гігроскопічної вологи; визначення зольності; визначення кількісного вмісту кальцію; визначення кількісного вмісту магнію; визначення кількісного вмісту заліза.

Ключові слова: лігнін, мікроскопічні дослідження, якісні реакції, властивості, вміст речовин.

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