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The effect of the industrial zone on the chemical composition of some medicinal plants

Biological characteristics of medicinal plants is largely determined by the place of their growth. This article presents the results of a study the influence of the industrial zone on the vegetation, the study of the influence of anthropogenic factors on the chemical composition of medicinal plants — hawthorn, sea buckthorn, yarrow growing in different conditions. The impact of industrial natural geotechnical systems is considered by the influence of JSC SSGPO (Sokolov-Sarbai Mining Production Association) and the adjacent territory of Rudny city. Sokolov-Sarbai Mining Production Association develops deposits of iron ore by open pit and underground methods. Analysis was performed with fruit, which is harvested from the territory of the industrial mining zone, and with fruit which is harvested on the rural territory, located at a more remote distance from the industrial zone, and pharmacy samples (Shymkent city). Alkalimetric method used for determining the total acidity of all samples. Qualitative analysis of organic acids was carried out by a method of paper chromatography, where the acids are extracted with a mixture of ether and acetone. The quantitative content of vitamin C (ascorbic acid) was determined by iodometric method. The quantitative content of tannins was determined by a permanganat-metric method. To confirm the presence of the iron, aluminum, calcium ions in samples harvested in the industrial area was determined by the ash content.

Keywords: medicinal plants, phytochemicals, hawthorn (Crataégus), sea Buckthorn (Hippóphaë rhamnoídes), yarrow (Achilléa millefólium), qualitative analysis, quantitative analysis, environment.

Nowadays, the problem of environmental protection is one of the most urgent. Certain contradictions in the interaction between society and nature are inevitable. The human society solves many civilization progress problems at the expense of the nature. People in the production process borrow everything what they need from the natural environment. Humankind has declared itself as a force and the power of an influence on the surface shell of the planet and today is almost equal to the cumulative effects of all living organisms. Every year, tens of millions of hectares of agricultural lands, forests are being destroyed. Thousands of species of animals and plants have disappeared. By today, the mining industry, especially open-pit mining is one of the most dangerous affects, influences for the environment and greatly impacts on nature. This entails a change in the landscape, the chemical composition of native plants.

Despite the emergence in the Arsenal of therapeutic agents in modern medicine and many synthetic antibiotic substances, interest in medicinal plants has not disappeared. Many higher plants accumulate organic substances used in pharmacology [1]. Biological characteristic of medicinal plants is largely determined by the place of their growth. In the harvesting of medicinal plants for the treatment and prevention of various diseases, it is necessary not only to know the specific characteristics of their properties, but also to procure medicinal raw materials correctly. We need to choose ecologically safe areas, not in contact with industrial zones, highways, building objects.

This article presents the results of a study the influence of the industrial zone on the vegetation, the study of the influence of anthropogenic factors on the chemical composition of medicinal plants — hawthorn, sea buckthorn, yarrow growing in different conditions.

The impact of industrial natural geotechnical systems is considered by the influence of JSC SSGPO (Sokolov-Sarbai Mining Production Association) and the adjacent territory of Rudny city, Kazakhstan. In this area there is a tension ecological situation, which was formed as a result of intense activity of the mining complex. Sokolov-Sarbai Mining Production Association develops deposits of iron ore by open pit and underground methods.

The chemical composition of medicinal plants (hawthorn, sea buckthorn, yarrow) native to Kostanay area (North part of Kazakhstan) today has not been studied thoroughly. In this regard, we have conducted chemical research of these medicinal plants. Hawthorn, sea buckthorn, yarrow — plants that are found on the territory of the industrial zone. These organisms can be considered to be as indicator organisms. Bioindication is a very good evaluation of the environment by the reaction of living organisms.

In traditional national medicine, the fruits and flowers of hawthorn is used for diseases of the heart, dizziness, shortness of breath, insomnia, diseases of the gastrointestinal tract, in gynecology. Hawthorn containing remedies are used in functional disorders of cardiac activity, if angioneurosis, atrial fibrillation and paroxysmal tachycardia. Hawthorn fruit harvested at maturity from late September until the first frosts. The chemical composition of the hawthorn has been well studied, e.g. in [2, 3].

Sea buckthorn blooms in April – May, before leafing or simultaneously with it. The fruits ripen in August – September. In fruits of sea buckthorn contains vitamins: ascorbic acid, carotenoids, tocopherols, thiamin, riboflavin, sterols, fatty and organic acids and other compounds [4, 5].

Yarrow herb has multilateral pharmacological properties due to the presence in medicinal raw material of various biologically active compounds. The leaves of the plant contain the alkaloid ahillein, essential oil which includes chamazulene; esters, camphor, thujone, borneol, glycosides of luteolin, tannins, resins, amino acids, organic acids, carotene, vitamin K, ascorbic acid, bitter substances [6, 7].

The collected materials were dried in air in the shade, in a ventilated room. During the preliminary analysis of aerial parts and fruits have been studied using qualitative reactions for the presence of organic acids, vitamin C, tannins, flavonoids.

Analysis was performed with hawthorn fruit, which is harvested from the territory of the industrial mining zone, and with hawthorn fruit which is harvested on the rural territory, located at a more remote distance from the industrial zone; yarrow herb, collected similarly from the territory of the industrial zone and from the rural territory as well. Pharmaceutical samples were also investigated (Shymkent city).

The leaves of the selected plants were removed from the plants, then washed under running tap water to remove dust. The plant samples were dried for few days and the leaves were crushed into the powder and stored in polythene bags for use. The powder was put into a test tube. Distilled water was added to the powder to soak it and shaken well, the solution then was filtered. The filtered extract of the selected plant samples were taken and used for further phytochemical analysis. Alkalimetric method used for determining the total acidity of all samples — hawthorn, sea buckthorn, yarrow.

For the quantitative determination of organic acids, the extraction was carried out with distilled water and titrated with 0.1 N solution of alkali. At account, it is necessary to take into account the amount of alkali consumed in the titration, and the amendment to the titer. The calculation is carried out as follows

$$X = \frac{a \cdot T \cdot 200 \cdot 10}{H \cdot 20},$$

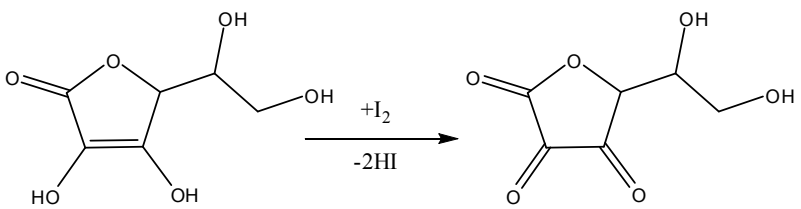
where a — amount of 0.1N NaOH, consumed in the titration, ml; T — the amendment to the alkali titer; 200 — the total volume of extract, ml; 20 — the volume of extract, spent for the titration, ml; H — weighed amount of substance, g; 10 — conversion into milli-equivalents of acids (1 ml of 0.1 N NaOH corresponds to 0.1 meq of acid); X — an amount of acids in plant sample, meq [2].

Qualitative analysis of organic acids was carried out by a method of paper chromatography, where the acids are extracted with a mixture of ether and acetone.

Analyzing the fruits of hawthorn, sea buckthorn, there has been determined the qualitative composition of the acid fractions by the method of ascending paper chromatography (R_f-value), with the use of special indicators of acids. As the mobile phase it was used the next mixture: *n*-butanol, formic acid, water. To prepare the mixture it was taken 250 ml of *n*-butanol, 25 ml of formic acid and 297 ml of water. All these solvents were transferred into a flask with a glass stopper, repeatedly shaken for several hours and allowed to settle during the day. After settling of mixture the top layer was used. (The upper layer of *n*-butanol, saturated with the formic acid).

The quantitative content of vitamin C (ascorbic acid) is determined by iodometric method in the fruits of hawthorn, sea buckthorn, and yarrow.

Ascorbic acid is a strong reducing agent. During the titration iodine it is oxidized to form dehydroascorbic acid:



Ascorbic acid dehydroascorbic acid

In the calculation of vitamin C content in the product was used, the formula for determining the mass using the titer determined by the substance:

$$M = \frac{n \cdot E}{1000} \cdot V ,$$

where n — is the molar equivalent concentration of iodine; E — the molar mass of equivalent of ascorbic acid in grams equal to in this case, 88 grams; V — is the volume used for titration of iodine in ml.

For recalculating the content of vitamin C in 100 g of the product, you must use the formula:

$$X = \frac{M \cdot 1000}{2} .$$

According to literature data among biologically active substances of the samples it was observed a high content of tannins. This plant polyphenolic compounds of different molecular weight, is able to tan the skin. Qualitative tests for tannins: 1) gelatin; 2) with acetate of lead; 3) with salesonline alum (JACQUES). All these reactions give positive results indicating the presence of tannins in the samples.

The quantitative content of tannins was determined by a permanganat-metric method.

A portion of the crushed material, sifted through a sieve with a hole diameter of 3 mm, placed in a conical flask with a capacity of 100 ml, poured 50 ml of boiling water and heated in a water bath for 30 minutes with frequent stirring. Liquid stand up for a few minutes and carefully filtered through cotton wool into a volumetric flask with a capacity of 250 ml so that the particles of the raw materials do not fall on the cotton wool. Raw materials in the flask repeatedly extracted with boiling water, as described above, the liquid filtered into the same volumetric flask. The extraction is repeated several times until a negative reaction for tannins (sample with a solution of alum gentoomaniac). The liquid in a volumetric flask is cooled, and the volume of extraction was adjusted to the mark with water. 25 ml of the resulting liquid placed in a conical flask with a capacity of 1 l, add 750 ml of water and 25 ml of indigenously and titrated with constant stirring 0.1 n potassium permanganate until a golden yellow colouring.

1 ml of 0.1 n potassium permanganate solution corresponds to 0,004157 g of tannins in terms of tannin. In parallel, perform a trial experiment, titrating 25 ml of indigenously in 750 ml of water [2]. The percentage content of tannins is determined by the formula:

$$X = \frac{(V_1 - V_2) KDV \cdot 100 \cdot 100}{mV_3 (100 - \omega)} ,$$

where V_1 — volume of 0.1 $KMnO_4$, used for titration, ml; V_2 — the volume of 0.1 $KMnO_4$ spent on control experience, ml; K — correction for the titer (for oxalic acid); D — coefficient for tannin for hydrolyzable tannins equals 0.004157, for condensed — 0.00582; V — is the total volume of extract, ml; m — is the mass of a sample of raw material, g; V_3 — volume of extract taken for titration, ml; ω — the loss in weight of raw material on drying, %.

To confirm the presence of the metals Fe, Mn in samples harvested in the industrial area was determined by the ash content of yarrow. Ash substances of vegetable raw materials is called the residue of inorganic substances generated after combustion of materials and subsequent calcination of the residue to constant mass. Plants ash (total ash) consists of a mixture of various inorganic substances in the plant and mineral contaminants that can get into the raw material at harvest and drying.

Ash often contains the following elements: K, Na, Mg, Ca, Fe, Si, P less often and in smaller amounts Cu, Mn, Al, etc.

Results and discussion

In order to identify organic acids, as an indicator solution was used Bromphenol blue solution (pH of 6.7). Organic acids are painted in bright yellow on a cyan background [2]. Results are presented in Table 1.

Table 1

Total acidity, quantitative content of vitamin C and quantitative content of tannins of the analyzed samples

Acids	Hawthorn		Buckthorn		Yarrow	
	Industrial zone	Rural zone	Industrial zone	Rural zone	Industrial zone	Rural zone
Organic acids, meq	19.2	32.0	19.3	34.7	3.4	6.0
Vitamin c, mg/100 g	14.0	26.4	450.0	700.0	140.0	240.0
Tannins, %	4.52	4.94	1.05	2.26	2.33	3.63

During the determination of the total acidity, there was determined that the least content of free acids are in the raw material gathered from the territory of the industrial zone. This was probably due to the high content of metal ions in the soil of the factory. These differences in the content of organic acids, we assume, are related to the fact that free acids can form poorly soluble salts with metal ions, and this is reflected in the decrease in the content of free acids in the samples taken closer to the industrial area.

Table 1 also shows that the amount of vitamin C in raw material harvested in the countryside, higher in comparison with samples collected near the industrial zone. This can be explained by the redox properties of ascorbic acid in the presence of iron ions (Fe^{2+}, Fe^{3+}) [2]. *L* — ascorbic acid is oxidized by ions of Fe^{3+}, respectively, this leads to a reduction in the concentration of vitamin C in samples of the industrial zone. On the other hand, the increase in humidity also contributes to the accumulation of vitamin C [3].

From these data we can conclude that the percentage content of tannins in the samples (Table 1) taken from the territory of the industrial zone is reduced. This is due to the ability of metal ions to reduce the content of tannins by precipitation. On the other hand, the increase in the content of tannins in the samples procured from rural areas can be explained by the hydrolysis of glycosides, phenolic compounds as tannins are derivatives of phenolic compounds. This can occur due to frequent watering.

The qualitative composition of organic acids hawthorn fruit and sea buckthorn varies (Table 2). In the fruit of a hawthorn collected from the industrial area, there are ascorbic acid, malic, citric, succinic. Whereas in the fruit of hawthorn, collected from rural areas, the presence of only ascorbic acid and citric acid. In fruits of sea buckthorn collected from the industrial area, there are ascorbic, malic, succinic acid. Suburban sea buckthorn contains only ascorbic acid and citric acid. These differences can be explained by processes occurring in the citric acid cycle (the Krebs cycle), as the acid composition in the fruits depends on the stages of the cycle.

Table 2

Qualitative composition of the acid fractions in the fruit of hawthorn, buckthorn

Acids	R_f	Hawthorn		Buckthorn	
		Industrial zone	Rural zone	Industrial zone	Rural zone
Ascorbic acid	0.28	+	+	+	+
Tartaric acid	0.42	–	–	–	–
Malic acid	0.58	+	–	+	–
Citric acid	0.60	+	+	–	+
Succinic acid	0.82	+	–	+	–

The ash content in the sample with industrial zones is higher than in the pharmacy specimen (Table 3). This confirms the assumption that the yarrow from the territory of industrial zones accumulate metals that can form compounds with organic acids. This is also confirmed by the solubility of ash in water; completely soluble only ash pharmacy sample, since it contains no heavy metals. Ash samples collected from industrial areas, partly dissolved in acetic acid and completely in concentrated nitric acid when heated, which indicates the contents in the grass of the insoluble carbonates and sulfates of elements such as iron, aluminum and calcium.

Table 3

Inorganic analysis of the yarrow pharmacy specimen

Mineral components of ash	Industrial zone	Drugstore samples
Ash	11.62	4.98
Cl^-	+	+
CO_3^{2-}	+	+
Fe^{3+}	+	–
Al^{3+}	+	–
Ca^{2+}	–	–

Conclusion

Thus, it was studied the influence of industrial natural geotechnical systems on the content of biologically active substances, of medicinal plants, growing near the Sokolov-Sarbai mining production association factory. The results of the analysis show that the least content of free acids, vitamin C and tannins are in the raw material collected from the territory of the industrial zone. It can be explained by the accumulation of harmful and polluting substances by plant organisms.

The assumption, that plants are collected from the territory of the industrial zones accumulate metals, is confirmed by the fact that the ash content in the specimen from industrial zones is higher than in the pharmacy specimen.

It is clearly traced that plants growing on the territory of the Sokolov-Sarbai mining production association factory, which is the zone of emissions of iron-containing waste, also contain an excessive amount of iron.

One of the important conclusions, that should be noted, is the fact that when harvesting medicinal plants, it is necessary to choose the right areas where it is possible to collect medicinal raw materials. For this, it is necessary to choose environmentally clean areas, free of the industrial pollutions, and do not contact industrial enterprises, motorways, mining enrichment plants.

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Дәрілік өсімдіктердің химиялық құрамына өндіріс орындарының әсері

Дәрілік өсімдіктердің биологиялық сипаттамасы негізінен олардың өсу ортасына тәуелді. Мақалада долана, шырғанақ, мыңжапырақ сияқты дәрілік өсімдіктердің химиялық құрамына өндіріс орындарының және антропологиялық факторлардың әсерін зерттеу жұмыстарының нәтижелері берілген. Өндірістік гео-техникалық жүйенің әсері Соколов-Сарыбай тау-кен өндірістік бірлестігінің (ОАО «ССГПО» – «ССТКӨБ» ААҚ) және соған жақын орналасқан Рудный қаласының маңайынан дайындалған дәрілік өсімдіктердің химиялық құрамын зерттеу нәтижесінде тұжырымдалған. Соколов-Сарыбай тау-кен өндірістік бірлестігі ашық және жабық тәсілмен темір кендерін өндіреді. Зерттеу үшін долана мен шырғанақтың жемістері және мыңжапырықтың жер беті бөлігі өндіріс орындарына жақын жерлерден, ал салыстыру үшін өндіріс аймағынан алыс орналасқан саяжайлардан дайындалды. Барлық сынамалардың жалпы қышқылдылығы алкалиметриялық әдіспен анықталды. Органикалық қышқылдардың сапалық құрамы қағаз бетіндегі хроматография әдісімен эфир мен ацетонның қоспасымен экстракция нәтижесінде жүргізілді. С дәруменінің мөлшері иодометриялық әдіспен (аскорбин қышқылы), танниндердің мөлшері перманганатометрия әдісімен анықталды. Өндіріс аумағынан жиналған сынамалардың құрамында темір, алюминий иондарының барлығын дәлелдеу үшін сынамалардың күліне сапалық талдау әдістеріндегі арнайы реакциялар қолданылды.

Кілт сөздер: дәрілік өсімдіктер, фитохимия, долана, шырғанақ, мыңжапырақ, сапалық талдау, сандық талдау, экология.

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Влияние промышленной зоны на химический состав лекарственных растений

Биологические характеристики лекарственных растений в значительной степени определяются местом их произрастания. В статье представлены результаты изучения влияния промышленной зоны на растительный покров, влияния антропогенных факторов на химический состав лекарственных растений — боярышника, облепихи крушиновидной, тысячелистника обыкновенного, произрастающих в различных условиях. Влияние промышленной природной геотехнической системы рассмотрено на примере ОАО «ССГПО» (Соколовско-Сарбайское горно-производственное объединение) и прилегающей территории города Рудного. Соколовско-Сарбайским горно-производственным объединением разрабатываются месторождения железных руд открытым и подземным способами. Для анализа использовались плоды боярышника и облепихи, которые заготавливали с территории промышленной зоны, и для сравнения собирали плоды на территории дач, находившихся на более отдаленном расстоянии от промышленной зоны; трава тысячелистника, собранная аналогично с территории промышленной зоны и с территории дач. Для определения общей кислотности всех образцов использовался алкалиметрический метод. Качественное определение органических кислот проводили методом бумажной хроматографии, для этого кислоты экстрагировали смесью эфира и ацетона. Количественное содержание витамина С (аскорбиновой кислоты) определяли йодометрическим методом. Количественное содержание танинов определяли методом перманганатометрии. Для подтверждения присутствия ионов металлов железа, алюминия, кальция в образцах, собранных в промышленной зоне, определяли зольность тысячелистника.

Ключевые слова: лекарственные растения, фитохимия, боярышник, облепиха крушиновидная, тысячелистник обыкновенный, качественный анализ, количественный анализ, экология.