Research on Grape and Fruit and Berry Wines and Detection of their Falsification

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DOI: 10.32353/khrife.2.2022.07 UDC 343.98:663.3
Submitted: 6 June 2022 / Reviewed: 16 June 2022 / Approved for Print: 17 June 2022 / Avialable online: 30 June 2022

Grape and fruit and berry wines were studied in order to detect signs of their falsification by adding synthetic dyes. It is noted that in the process of analysis (examination) of unknown liquids provided for research, specialists must first of all establish the nature of such objects. It is possible to find out only after identifying the spectrum of features characteristic of the object in its actual state. The list of organic acids, which are components of grape and fruit and berry wines, was established experimentally; the possibility of determining organic acids in the analyzed samples was proven; signs of falsification of wines with the addition of dyes were given and methods of their detection were proposed. One of the cornerstone requirements for forensic examination is the mandatory confirmation of the results of analysis by at least two reliable methods, therefore, in the proposed scientific research, options for the study of some synthetic dyes

This article is translation of the original Ukrainian content, which source is available at the link: *https://khrife-journal.org/index.php/journal* (translated by Tetiana Droshchenko). The author acknowledges translation as corresponding to the original.

using methods of thin-layer chromatography, IR spectroscopy and the addition of alkaline solutions are considered. It was established that the set of specific organic acids in grape and fruit and berry wines, which can be detected using the chromatography method, makes it possible to use them as differential signs in the process of establishing the nature of the wine. Samples of real grape wines are marked by a high concentration of tartaric acid, which is present only in grape products. It has been proven that the set of methods for studying grape and fruit and berry wines, aimed at determining the presence and identification of synthetic dyes, makes it possible to answer the questions posed by the examination on the falsification of winemaking products by coloring.

Keywords: *organic acids; thin-layer chromatography; grape must; solvent systems; wine color; chromatographic mobility; synthetic dyes; sorting; falsification.*

Research Problem Formulation

During the study of unknown liquids received for research, experts must first of all establish the nature of the research object. It is possible to determine this only under the condition of identifying features characteristic of a specific object in its actual state. For fruit and berry juices (as well as drinks made from them), such features can be organic acids, which (to a greater extent than any other compounds) determine the taste characteristic of mentioned juices.

Analysis of Recent Researches and Publications

Some researchers believe that the identification indicators of wine should be based on the search for natural compounds, characteristic or uncharacteristic for this type of product, as well as on the search for chemicals of natural or synthetic origin, deliberately added to the drink to give it the desired properties for the purpose of falsification [1]. Thus, M. H. Markovskyi [2] proposes to carry out an examination of

1 Агеева Н. М., Гугучкина Т. И., Марковский М. Г. Критерии оценки фальсифицированности виноградных вин. *Известия ВУЗов. Пищевая технология*. 2002. № 2—3. С. 84—86 ; Герасимов М. А. Технология вина. Москва, 1959. 642 с. ; Бабаева М. В., Панасюк А. Л., Кузьмина Е. И. Соотношение основных компонентов экстракта красных вин. *Виноделие и виноградарство*. 2014. № 1. С. 18—20 ; Нилов В. И., Скурихин И. М. Химия виноделия. 2-е изд., доп. и перераб. Москва, 1967. 442 с. ; Charters St., Pettigrew S. Conceptualizing product quality: the case of wine. *Marketing Theory*. 2006. V. 6. Is. 4. P. 467—483. DOI: 10.1177/1470593106069932 (date accessed: 04.06.2022).

2 Марковский М. Г. Оптимизация определения органических кислот вина методом капиллярного электрофореза. *Новации и эффективность производственных процессов в виноградарстве и виноделии*. 2005. Т. 2. С. 242—246 ; Методика оценки подлинности вина. Белые сухие вина и виноматериалы: РД 50.27.15.18/0003-99. Краснодар, 1999. 13 с. (Государственная система обеспечения единства измерений).

wines to confirm their naturalness by the proportion of bound organic acids, which in natural wines (according to the scientist) is more than 90 %, and in falsified products does not exceed 10 %. Some researchers are convinced that it is necessary to use a set of indicators to detect falsification: quality composition and content of amino acids; presence and concentration of glycerol; ratio of concentrations of free and bound forms of organic acids; given extract [3]. So, it is believed that real wines are characterized by the ratios *"mass concentration of tartaric acid / mass concentration of citric acid"* in the range of 6.2:1...21:1 and *"mass concentration of tartaric acid / mass concentration of malic acid"* within 1.1:1...5,3:1 [4]. However, to this day, the forensic literature lacks information on conducting examination in this direction.

Drinks made from fruits and berries contain a variety of acids, but only one of them can predominate in each type. For instance, apples contain: malic, citric, succinic, adipic, α-ketoglutaric, oxaloacetic, pyruvic, acetic, chlorogenic and other acids. In general, this is due to the presence of only a few acids, namely: approximately 70 % is malic acid; up to 20 % — citric; almost 7 % — succinic and only up to 3 % — the rest of acids. Malic acid also prevails in other grain and stone fruits, and in most berries. Citrus fruits have more citric acid.

In grape must and wines, organic acids are represented by tartaric, malic, citric, succinic, oxalic, lactic, glycolic, glucuronic, salicylic and some other acids, which may be present in trace amounts and which cannot always be detected. However, the content of tartaric and malic acids in grape must and wine is the highest; in addition, it is known that tartaric acid is found in significant quantities only in grapes, that is a specific component of grape juice and wine, and is not contained in fruit and berry wines.

Lactic (0.5—6.3 g/dm^3) and (in slightly smaller amounts) succinic (0.24—1.5 g/dm^3) acids are detected in grape wines in fairly significant quantities. Citric acid contained in must (from traces to 0.7 g/dm^3) is not a permanent and stable component of wine due to its easy destruction by bacteria, so it cannot always be detected in grape wines. In addition to the above, other acids can be detected in various wines, mainly in the form of traces: benzoic acid, dimethylglycerin acid, galacturonic acid, gluconic acid, glutamic acid, malonic acid, oxalic acid, hydrogen cyanide, phosphoric acid, hydrogen chloride, etc.

Diluting grape wine with cheap fruit and berry or other drinks to increase its volume is the most common and at the same time crude method of falsification. As a result, the intensity of color changes, the saturation of the bouquet, and the strength of wine decreases. For the most part, such wines are *"corrected"* by adding various chemical components (alcohol, more often technical, containing fusel oils; sugar substitutes; artificial dyes, etc.).

3 Бабаева М. В., Панасюк А. Л., Кузьмина Е. И. Op. cit. ; Зотов А. Н., Аникина Н. С., Зинькевич Э. Л. Система контроля качества вина в странах старого и нового света. *Формирование национальной системы качества винопродукции* : междунар. форум. Одесса, 2013. С. 14—15 ; Марковский М. Г. Совершенствование технологии и методов оценки качества виноградных вин на основе анализа и регулирования их кислотного состава : автореф. дис. ... канд. техн. наук. Краснодар, 2006. 24 с.

4 Кишковский З. Н., Мержаниан А. А. Технология вина : учебн. пособ. для студ-в вузов пищев. пром. Москва, 1984. 439 с.

Galization of wine as a method of falsification consists in the fact that sour wines are *"improved"* by adding water to a known volume, followed by bringing the strength and acidity to certain limits, regulated by the current standard.

Chaptalization of wine is a method of processing sour must with alkaline agents and adding sugar before or during fermentation.

Petiotization of wine is a method of obtaining wine by infusing and fermenting sugar syrup on the pomace remaining after the separation of grape juice.

Shellification, or the addition of glycerin, is used to reduce acidity and bitterness, increase sweetness, and to stop the fermentation process.

The use of preservatives (salicylic acid, other antiseptics) in order to speed up the technological process.

Forgery of a bouquet of wine. For this, mixtures of various complex esters (enanthic, valerian, valerian-amyl, butyric, etc.) are used, as well as dried grape flowers.

Falsification of the production method. Wines produced in violation of the technological scheme developed and approved for the current designation of wines are considered high-quality. This type of falsification is quite difficult to recognize, moreover, it is quite diverse in methods and means, for example:

- varietal wines are replaced by blended wines;
- different fractions of must are mixed;
- the aging period of the wine is falsified;
- *"artificial wines"* are made. Grape juice is not required for making such wines, as they are a well-chosen mixture of components (water, yeast, sugar, tartaric potassium, crystalline tartaric and citric acids, tannin, glycerin, ethyl alcohol, enanthate ether, etc.), which the consumer organoleptically perceived as grape wine.

Wine coloring is used to hide other forgeries (for example, dilution) or to recolor certain varieties of low-value white wines into red. For this, natural (elder berries, blueberries, aqueous beetroot infusion, etc.) and synthetic dyes (aniline, naphthalene, anthracene dyes, indigo carmine, fuchsin) are used, many of which are not only harmful, but even poisonous compounds (for example, fuchsin).

A wide range of methods for studying and identifying the main organic acids in wines is given in the literature. The authors offer both fairly simple types of examinations, including the addition of alkaline solutions, thin-layer chromatography [5], and complex instrumental methods: ultrasonic monitoring [6], the use of electrochemical biosensors [7], IR spectroscopy [8], capillary

5 Samarasekara D., Hill C., Misna D. Analysis and Identification of Major Organic Acids in Wine and Fruit Juices by Paper Chromatography. *Journal of Chemical Education.* 2018. Vol. 95. Is. 9. Pp. 1621—1625. DOI: 10.1021/acs.jchemed.8b00129 (date accessed: 04.06.2022).

6 Novoa-Diaz D., Rodriquz-Nogales J. M., Fernandez-Fernandez E., Vila-Crespo J., Garcia-Alvarez J., Amer M. A. & all. Ultrasonic monitoring of malolactic fermentation in red wines. *Ultrasonics*. 2014, Aug. Vol. 54. Is. 6. Pp. 1575—1580. DOI: 10.1016/j.ultras.2014.04.004 (date accessed: 04.06.2022).

7 Gimenez-Gomez P., Gutierres-Capitan M., Capdevila F., Puig-Pujol A., Fernandez-Sanchez C., Jimenez-Jorquera C. Monitoring of malolactic fermentation in wine using an electrochemical bienzymatic biosensor for L-lactate with long term stability. *Analytica Chimica Acta*. 2016, Jan 28. Vol. 905. Pp. 126—133. DOI: 10.016/j.aca.2015.11.032 (date accessed: 04.06.2022).

8 Regmi U., Palma M., Barroso C. G. Direct determination of organic acids in wine and wine-

electrophoresis [9], high-performance liquid chromatography (HPLC) [10], ^{1}H-NMR spectroscopy [11].

The application in expert practice of methods for identifying the complex of basic organic acids contained in wines (oxalic, citric, malic, amber, adipic, lactic, in particular, tartaric acid — characteristics specific to grape wines), and identifying, establishing the types of dyes will allow not only to establish the nature (origin) of the unknown liquid submitted for examination, but also to differentiate grape and fruit and berry wines in the event of their sorting or mixing.

Article Purpose

Research grape and fruit and berry wines, as well as to identify signs of their falsification by adding synthetic dyes.

Main Content Presentation

Preparation for conducting the examination

Solutions of organic acids -"witnesses". A mixture of organic acids: oxalic, citric, tartaric, malic, succinic, adipic, lactic, prepared at a concentration of 5 mg/cm^3 of each acid (aqueous solution), is taken as a standard sample. Solutions of individual acids can be prepared in the same concentration (if necessary).

Solvents. A solvent system is recommended: ethanol — ammonia — water in a volume ratio of 50:15:2.5. The solvent system is used for chromatography immediately after preparation. Before immersing plates, the hermetically sealed container with the introduced system is vigorously shaken to saturate it with solvent vapors.

Developer. 2 cm^3 of freshly distilled (colorless) aniline is dissolved in 20 cm^3 of ethanol, and 2 g of l-arabinose (other carbohydrates can also be used) in 20 cm^3 of distilled water. The two obtained solutions are poured together and the volume is brought to 100 cm^3 with butanol. A chromatogram is developed with the prepared mixture using a sprayer.

Examination of liquids for the presence of organic acids by the method of chromatography in a thin layer of sorbent

Apply 5 mm^3 of wine (an unknown liquid sample) to a plate with a thin layer of

derived products by Fourier transform infrared (FT-IR) spectroscopy and chemometric techniques. *Analytica Chimica Acta*. 2012, June 30. Vol. 732. Pp. 137—144. DOI: 10.1016/j.aca.2011.11.009 (date accessed: 04.06.2022).

9 Coelho C., Bagala F., Gougeon R. D., Schmitt-Kopplin Ph. Capillary Electrophoresis in Wine Science // Methods in Molecular Biology. Series Editor Walker J. M. 2016. MIMB, Vol. 1483. Pp. 509—523. DOI: 10.1007/978-1-4939-6403-1_23 (date accessed: 04.06.2022).

10 Eyéghé-Bickong H. A., Alexandersson E. O., Gouws L. M., Young Ph. R., Vivier M. A. Optimisation of an HPLC method for the simultaneous quantification of the major sugars and organic acids in grapevine berries. *Journal of Chromatography B*. 2012, Feb 15. Vol. 885—886. Pp. 43—49. DOI: 10.1016/j.jchromb.2011.12.011 (date accessed: 04.06.2022) ; Perez-Ruiz T., Martinez-Lozano C., Tomas V., Martin J. High-performance liquid chromatographic separation of citric, lactic, malic, oxalic and tartaric acids using a post-column photochemical reaction and chemiluminescence detection. *Journal of Chromatography A*. 2004. Feb 13. Vol. 1026. Is. 1—2. Pp. 57—64. DOI: 10.1016/j.chroma.2003.10.130 (date accessed: 04.06.2022).

11 Avenoza A., Busto J. H., Canal N., Peregrina J. M. Time course of the evolution of malic and lactic acids in the alcoholic and malolactic fermentation of grape must by quantitative ^{1}H NMR (qHNMR) spectroscopy. *Journal of Agricultural and Food Chemistry*. 2006, Jun 7. Vol. 54. Is. 13. Pp. 4715—4720. DOI: 10.1021/jf060778p (date accessed: 04.06.2022).

sorbent — *Sorbfil* — measuring 15×10 cm. After each touch of the capillary to the plate, the resulting stain is dried with a stream of warm air. In the same way, 2—3 mm^3 of a standard solution of a mixture of organic acids (8—10 touches of the capillary) are applied next to the spots of the sample under examination [12].

A plate ready for chromatography is immersed in the solvent system: ethanol — ammonia — water (50:15:2.5). The chromatography process lasts 75-90 minutes. Then the plate is removed from the container, dried for 3-4 hours. After complete removal of the solvent, the plate is re-immersed in a freshly prepared solvent system and the process is repeated. The plate dried after the repeated chromatography process is moistened with a developer reagent from the sprayer under draft.

To develop the color of spots, the chromatogram is placed in a thermostat at a temperature of 100—110 °C. In 10—15 minutes, dark brown spots appear on a light yellow background, which retain their color for a long time at room temperature. The chromatogram is evaluated by the method of visual comparison.

The examination of wines using the specified system of solvents makes it possible to detect on chromatograms up to 10-11 acids, the presence of which in complex biological systems (such as wines) is not excluded.

Table 1 shows approximate R_f values for organic acids that can be detected in grape and fruit and berry wines.

Table 1

Rf values of organic acids that can be detected in wines

Acids	**System: ethanol — ammonia — water, R_f**
Oxalic	0,00
Citric	0,14
Tartaric	0,31
Malic	0,44
Amber	0,56
Adipic	0,68
Glycolic	Not detected
Lactic	0,82

Note. The nature of the distribution of spots on chromatograms and their sequence remain unchanged.

It should be noted that the solvent system benzene — ethanol — ammonia (10:20:5) can be used for chromatography, but the spots of organic acids in such a solvent system are located close to each other, which makes it difficult to identify the acids on the chromatogram. Considering the above, it is worth recommending the eluent system ethanol — ammonia — water (50:15:2.5).

The chromatogram of pure organic acids is shown in fig. 1.

12 Гейсс Ф. Основы тонкослойной хроматографии : в 2-х т. : пер. с англ. / под ред. В. Г. Березкина. Т. 1. Москва, 1988. 404 с.

Fig. 1. Chromatogram of pure organic acids in the system: ethanol — ammonia — water (50:15:2.5). Acids: 1 — oxalic; 2 — citric; 3 — tartaric; 4 — malic; 5 — amber; 6 — adipic; 7 — lactic

Evaluating the results of testing liquids for the presence of organic acids

When testing unknown grape and berry wines, it is difficult to predict in advance the composition and quantitative content or ratio of individual acids in the sample, so the amount of wine that the expert puts on the plate is not always equal to 5 mm^3. In some cases, wines contain significantly more of one acid than other acids, for example, malic. One under such conditions, the application of 5 mm^3 will cause overloading of the sorbent with this acid, which will distort the chromatographic pattern. If the concentration of detected components of the examined samples does not correspond to the concentrations of the acids of the compared reference mixture, then inaccuracies are possible during the evaluation of chromatograms. In this case, the amount of wine to be applied to the plate must be reduced to 2.5—3 mm^3, but to such an amount as to be able to detect other acids, the amount of which is very small.

Separately, we should note that a standard mixture of acids — *"witnesses"* — must be applied to the plate next to the stain of the sample under examination: for a more correct and clear identification of individual acids. The objects of our research are expert samples of "*Margrani"* red wine, *"Somersby"* cider, and *"Somersby Watermelon"*. The chromatogram of grape red wine *"Margrani",* apple cider *"Somersby"* and a mixture of organic acids is shown in fig. 2.

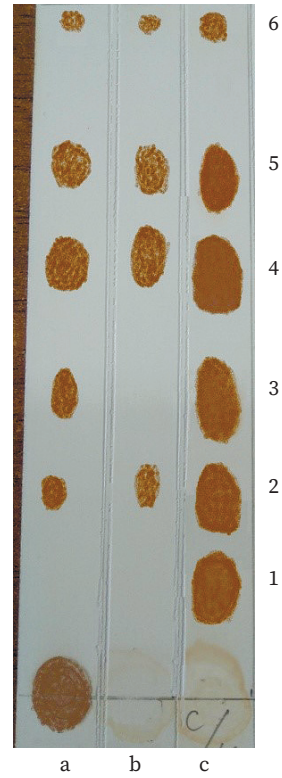


Fig. 2. Chromatogram for the examined samples: a) "*Margrani"*; b) apple cider *"Somersby"*; c) acids for comparison (1 — oxalic; 2 — citric; 3 — tartaric; 4 — malic; 5 — amber; 6 — lactic)

Chromatographic picture in fig. 2 is an example of a typical picture for grape and fruit and berry wines. Grape wines are characterized by the presence of tartaric and malic acids in much greater quantities than the rest of acids. Sometimes the malic acid predominates the tartaric one.

In most grape wines, citric acid is either absent or present in very small amounts; amber acid is detected in small amounts; between the spots of citric and tartaric acids, a spot of an unidentified acid is observed. In addition, oxalic acid, if it is present in wines, is at the start, possibly in a mixture with other acids. Near the start, many fortified wines have a stain of unidentified acid. Lactic acid is always detected near the solvent front.

It should be noted that the typical chromatographic pattern of fruit and berry wines is characterized by the absence of tartaric acid. For the most part, in fruit and berry wines, an unidentified acid ($R_f = 0.2$) is absent or appears as traces, which is clearly observed in grape wines (placed on the chromatogram between citric and tartaric acids).

Most fruit and berry wines (from cranberries, red and black currants, strawberries, black rowan, plums, gooseberries, raspberries, etc.) contain quite a lot of citric acid. Malic acid is well detected (it is present in significant quantities in apple wines). Unlike grape wines, fruit and berry wines contain a significant percentage of amber acid; adipic and one or two unidentified acids placed between amber and lactic acids may be detected.

The set of specific organic acids in grape and fruit and berry wines, which are detected by experts using the chromatography method, makes it possible to use them as differential signs in the process of establishing the nature of the wine. Samples of real grape wines are characterized by a high concentration of tartaric acid, which is present only in grape products. In samples of fruit and berry wines made from apricot, raspberry and plum fruits, the main component is malic acid.

During the examination of home-made grape wines, the absence of tartaric acid can serve as evidence of wine falsification, that is, its production from grape pomace, sugar, water. Such wines also lack malic acid.

Using the considered method of chromatography in a thin layer of sorbent, it is quite difficult to examine wines containing sugar, especially when its content is significant. Therefore, the examination of fortified wines should be preceded by work on the separation of organic acids on ion-exchange resins, after which the obtained eluates are chromatographed in a thin layer of sorbent.

The color characteristics of wine products are quite variable — depending on the type of raw materials, technological production, composition of the blend. This feature is used by some unscrupulous producers, often using cheaper fruit and berry raw materials to tint grape wines.

Natural food dyes are obtained from plant raw materials (flowers, leaves, berries, root crops) and waste from wineries and canneries. Natural dyes most often belong to carotenoids and flavonoids.

Synthetic food dyes are complex organic substances obtained by a chemical method. Unlike natural ones, they do not contain flavors and vitamins. Compared to natural dyes, synthetic ones give bright saturated tones that are less sensitive to storage conditions. Inorganic food dyes

are obtained from mineral raw materials of natural or chemical origin. These include some finely dispersed metals and metal oxides (hydroxides), amorphous carbon (E152, E153), calcium carbonate, as well as blue pigment (ultramarine).

One of the requirements for forensic examination is mandatory confirmation of analysis results by at least two reliable methods, so in our research we consider the option of examination some synthetic dyes using the method of thin-layer chromatography and IR spectroscopy. Research objects are expert samples of synthetic dyes: azorubine (carmoisin; E122), a mixture of azorubine (E122) and Ponceau 4R (E124), yellow *"sunset"* (E110), tartrazine (E102), samples of red wine *"Margrani"*, *"Somersby"* and *"Somersby Watermelon"* cider, *"Ripe Cherry"* and *"Peach"* alcoholic beverages. Experts also prepared a model mixture of *"Somersby Watermelon"* cider with synthetic dyes E122, E124.

Detection of synthetic dyes by adding an alkaline solution

Synthetic dyes can be detected by adding an alkaline solution (ammonia, soda) in an amount that exceeds the amount of the drink. A change in the pH leads to a change in the color of natural dyes: red to dirty blue, violet to red-brown. If the liquid has a yellow, yellow-hot or green color, then after adding alkali, the mixtures must be boiled. Such pigments as carotenoids and chlorophyll are destroyed. At the same time, yellow and yellow-hot colors disappear, and green turns into brown or dark green. The color of synthetic dyes does not change under these conditions. Thus, the color of the wine *"Margrani"* bordeaux in the case of adding soda solution changed to blue-green, and the deep red color of the model mixture (*"Somersby Watermelon"* cider with synthetic dyes E122, E124) did not change after adding soda solution (*see Fig. 3*). A sample of *"Somersby Watermelon"* cider, in the composition of which the manufacturer noted sugar color III, changed its color from pink to pale yellow (almost colorless) with the addition of soda solution (*see Fig. 4*).

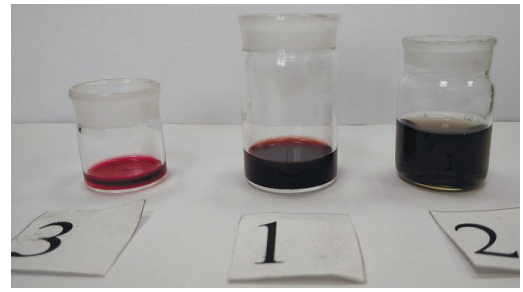


Fig. 3. 1 — red wine *"Margrani";* 2 — red wine *"Margrani"* with addition of soda solution; 3 — a sample of the mixture of *"Somersby"* cider, E122, E124 with the addition of soda solution

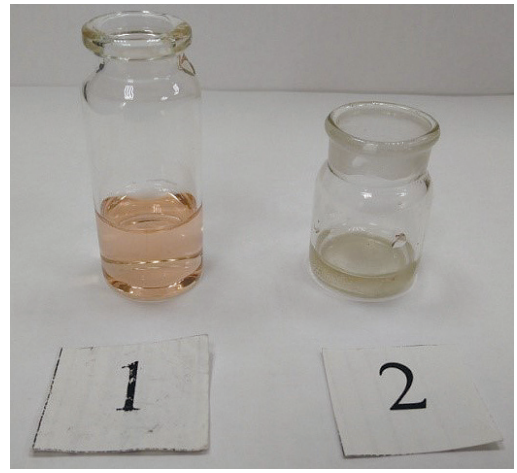


Fig. 4. 1 — a sample of *"Somersby Watermelon"* cider; 2 — a sample of *"Somersby Watermelon"* mixture with the addition of soda solution

This method makes it possible to answer the question about the presence of synthetic dyes in their composition in principle and quickly at the preliminary stages of winemaking product examination.

Examination of liquids for the presence of synthetic dyes by thin-layer chromatography

Thin-layer chromatography (due to its accessibility, simplicity and expressivity) is widely used for the analysis of dyes. Synthetic dyes form colored spots on chromatographic plates clearly visible to the naked eye, which helps the expert to visually evaluate the obtained results.

As of today, it is impossible to choose universal separation conditions for most dyes. This is due to the fact that food synthetic dyes have close *Rf* values that tightly fill almost the entire possible interval (*Rf* = 0.10...0.95), which is a significant obstacle for thin-layer chromatography with high resolution.

To determine the qualitative composition of individual and mixed synthetic dyes, the researchers used the following systems:

1) n-propanol — ethyl acetate — ammonia — water (10:3:3:0.1);
2) isobutanol — ethanol — ammonia — water (1:2:0.1:1).

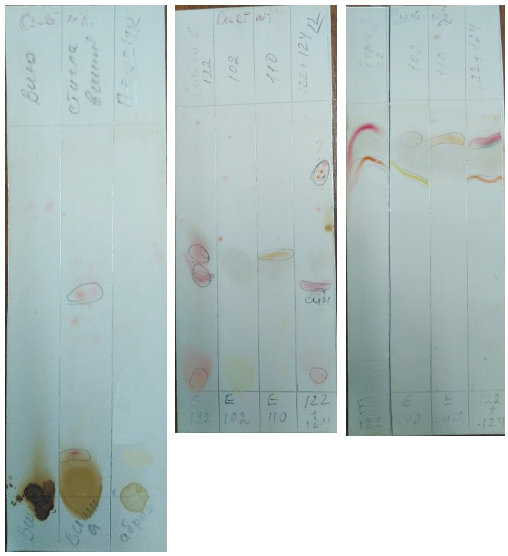
Two solvent systems were used to separate dyes with similar values of chromatographic mobility, and also as reference to each other. Chromatographic properties of dyes in different systems are shown in tbl 2.

Table 2

Chromatographic properties of dyes in different systems

Name of the dye	System No. 1		System No. 2	
	R_f	Color of chromatographic zones	R_f	Color of chromatographic zones
Azorubine (E122)	0,35	Crimson	0,80	Orange
			0,92	Crimson
Ponceau 4R (E124)	0,76	Red-crimson	0,84	Violet
Tartrazine (E102)	0,11	Yellow	0,75	Bright yellow
Yellow *"sunset"* (E110)	0,46	Yellow-hot	0,82	Orange

To check the reliability of the method, the examination was conducted: red wine *"Margrani"*, alcoholic beverages *"Ripe cherry"* and *"Peach"*. Chromatography was performed in the solvent system n-propanol — ethyl acetate — ammonia — water (10:3:3:0.1): *see Fig. 5a*.



5a 5b 5c

Fig. 5. 5a) — chromatogram of red wine *"Margrani"*, alcoholic beverages *"Ripe cherry"* and *"Peach"* (from left to right) in eluent system No. 1; 5b) — chromatogram of synthetic dyes E122, E102, E110, E122 + E124 (from left to right) in eluent system No. 1; 5c) — chromatogram of synthetic dyes E122, E102, E110, E122 + E124 (from left to right) in eluent system No. 2

As a result of the examination, it was established that:

- the chromatogram with the examined sample of *"Margrani"* red wine does not contain colored zones, that is, there are no dyes;
- the chromatograms of *"Ripe cherry"* drink showed orange and crimson spots, which in terms of color and chromatographic mobility correspond to the synthetic dye azorubine (E122);
- a yellow spot appeared on the chromatogram of *"Peach"* drink, which in terms of color and chromatographic mobility corresponds to the synthetic dye tartrazine (E102).

The above thin-layer chromatography method requires samples for comparison. In the absence of reference samples, it is difficult to obtain reliable information about the nature and component composition of the examined dyes, so there is a need to apply additional research methods. To perform a number of practical tasks, you can use the IR spectroscopy method, which allows you to identify the object under examination with the help of computer information and search systems, spectral libraries and reference information. For this, preliminary preparation of samples aimed at separating the dye from the examined mixture is necessary.

Examination of liquids for the presence of synthetic dyes by IR spectroscopy

Sample preparation. The method of solid-phase extraction followed by evaporation of the extract to a dry residue is used to isolate synthetic dyes. Spectra were recorded on a spectrophotometer *NICOLET — 380 SMARTPERFORMER* attachment manufactured by *Thermo Electron Corporation* (USA) under standard conditions.

Analysis parameters:

- measurement range — 650—4000 cm^{-1};
- resolution — 4;
- recording speed — 0,6329;
- amplification — 4;
- number of scans — 32.

The obtained spectra were analyzed by exemining the shape, position, and relative intensities of the characteristic absorption bands with the help of databases (electronic spectral libraries), as well as reference materials and special literature. At the same time, it was proved that dyes of different types differ from each other in IR spectra and can be differentiated.

Conclusions

It has been proven that the application in expert practice of methods for detecting the complex of basic organic acids contained in wines (oxalic, citric, malic, amber, adipic, lactic, as well as tartaric as specific for grape wines) made it possible not only to establish the nature (origin) of an unknown liquid submitted for examination, but to differentiate grape and fruit and berry wines in case of their re-sorting or mixing.

It was established that the set of specific organic acids in grape and fruit and berry wines, which can be detected using the chromatography method, makes it possible to use them as differential signs in the process of determining the nature of wine. Samples of real grape wines are characterized by a high concentration of tartaric acid, which is present only in grape products.

It has been proven that a set of methods for researching grape and fruit and berry wines, aimed at determining the presence and identification of synthetic dyes, makes it possible to answer the questions of experts on the falsification of winemaking products by coloring.

Дослідження виноградних і плодово-ягідних вин та виявлення їх фальсифікації

Алла Клімчук, Ольга Буй, Хосе Мануель Колодрас, Ольга Пашкова

Досліджено виноградні та плодово-ягідні вина з метою виявити ознаки їх фальсифікації шляхом додавання синтетичних барвників. Зазначено, що у процесі аналізування (експертизи) невідомих рідин, наданих для дослідження, фахівцям насамперед необхідно встановити природу таких об'єктів. З'ясувати це можливо тільки після виявлення спектра ознак, характерних для об'єкта в реально існуючому стані. Дослідним шляхом установлено перелік органічних кислот, що є складовими виноградних і плодово-ягідних вин; доведено можливість визначення органічних кислот в аналізованих зразках; наведено ознаки фальсифікації вин за допомогою додавання барвників і запропоновано методи їх виявлення. Одна з наріжних вимог до судової експертизи — обов'язкове підтвердження результатів аналізу не менш ніж двома достовірними методами, тому в запропонованій науковій праці розглянуто варіанти дослідження деяких синтетичних барвників із застосуванням методів тонкошарової хроматографії, ІЧ-спектроскопії та додаванням лужних розчинів. Констатовано, що сукупність конкретних органічних кислот у виноградних і плодово-ягідних винах, які можна виявити за допомогою методу хроматографії, дає змогу використовувати їх як диференційні ознаки у процесі встановлення природи вина. Зразки справжніх виноградних вин відзначено високою концентрацією винної кислоти, наявної лише у виноградній продукції. Доведено, що комплекс методів дослідження виноградних і плодово-ягідних вин, спрямованих на визначення наявності й ідентифікацію синтетичних барвників, дає змогу відповісти на питання, поставлені на вирішення експертизи про фальсифікацію продуктів виноробства шляхом забарвлення.

Ключові слова: *органічні кислоти; тонкошарова хроматографія; виноградне сусло; системи розчинників; колір вина; хроматографічна рухливість; синтетичні барвники; пересортиця; фальсифікація.*

Funding
This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Disclaimer
The funders had no role in the study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Contributors

The authors contributed solely to the intellectual discussion underlying this paper, case-law exploration, writing and editing, and accept responsibility for the content and interpretation.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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