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Influence of raw materials and distillation equipment on the heavy metal content of waste from an alcoholic anis-type beverage

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Abstract

This study focused on the heavy metal content waste resulting from the production of an anis-type beverage. Although natural ingredients were used in the production process, the waste contains heavy metals and is considered hazardous. Several metals were found in the waste (Fe, Cu, Ni, Zn, Cr and Cd), with concentrations of Fe to 157.5, Cu to 82.5, Zn to 31 and Ni to 8.5 mg/l. To collect information on the source of these metals, the residues of the herbs used for flavoring were examined for processes employing metallic and non-metallic pot stills. Herbs distillation residues were found to contain metals in non-metallic stills, e.g. aniseed residues from glass stills contained Cu up to 1.02 and Ni up to 0.9 mg/l. Fennel residues contained Ni up to 1.2 and Zn up to 6.6 mg/l. The main source for the metals was the bronze pot stills. The metals were in complexed form in the solution. The existence of metals in the amorphous phase as shown by a SEM micrograph indicates forming of metal–organic complexes, also verified by HPLC. Complexation data can be used for selecting the proper wash treatment method. The formation of large molecules favors precipitation and chemi-sorption treatment methods.

Keywords: Aqueous waste; Heavy metals; Complexes formation in residues; Pot stills corrosion; Anis-type beverage

1. Introduction

Anis-type spirits are produced by the distillation of pressed fermented grapes, dregs and other fermented saccharate raw materials, flavored with *aniseed* (*Pimpinella anisum* I) and/or *fennel* (*Foeniculum vulgare*) and other herbs. Production of anis-type spirits normally

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is a batch process utilizing bronze pot still distillation of aromatic herbs contained in a sack with water–alcohol solutions [1]. The waste of this process is a solution that includes the *flegmes* (i.e. "heads" and "tails") of the distillation, the residues and the rinse water from the pot stills when the sack containing the aromatic herbs is removed.

The use of natural ingredients, i.e. herbs, water and ethyl alcohol in the beverage, should not suggest the formation of a hazardous waste during the production process. It was found, though, that the waste contains heavy metals [2]. The waste which contained a significant concentration of metals, such as Cu, Fe, Ni, Zn, Cd and Cr is considered hazardous, requiring treatment before disposal [3]. Part of the metal content is attributed to the production process and another part to the flavoring herbs and combined use of metallic pot stills.

The organic compounds, especially organic acids, extracted from the herbs, as shown using high performance liquid chromatography (HPLC), enhance the corrosion of the metallic pot stills during distillation. Metals cannot be detected in the beverage and the formation of complexes in the residue is discussed. Wave dispersive X-ray analysis (WDXA) combined with scanning electron microscope (SEM) can provide information about the distribution of heavy metals and other elements in the various particles in the waste, as this analytical technique has the unique advantage of allowing microscopic components of heterogeneous materials to be selected visually and then individually analyzed for a wide range of metallic elements [4–7]. Study utilizing HPLC chromatograms of glass still residue and residue with added metal indicates the formation of metal–organic complexes, verifying the participation of the metallic construction material of traditional bronze pot stills [8].

Much of the published information on anis-type drinks (these include: *pastis* (France); *anesone* (Spain); *sambuca* (Italy); *zebib* (Egypt); *arak* (Syria); *ouzo* (Greece) etc.) was focused on the production process and its chemistry utilizing relatively crude methods such as analysis of bulk samples. Thus, our understanding of the production process and its byproducts is largely confined to gross properties, and to characteristics of certain isolated types of anis drinks. In-depth investigation of such systems has been hampered, however, by limitation of information (i.e. patented synthesis of beverages). This limitation is yet a problem for full exploitation of data herein.

This study was specifically conducted to address the following points:

1. To confirm and identify the metal accumulation and its origin in the waste of the process, with emphasis to the spirit *ouzo*.
2. To collect information on each type of raw material used for the production of the spirit, i.e. metal content, pH.
3. To investigate the form in which the metal content is present in the waste and the reasons why it is hazardous to the environment.
4. To evaluate the results, with special reference to their potential use in developing technologies for waste treatment.

2. Materials and methods

2.1. Aromatic herbs and waste sampling

The production capacity of the distillation unit involved in the study was 5,000 m^3 per year. The resulting waste produced was 12,000–15,000 kg. Waste samples were obtained

from the 1000 kg temporary storage tank by taking three samples when it was one-third full, half-full and totally full.

In total, 18 plant samples of nine species of herbs including shoots, stems, seeds and blooms were collected. Plants were sampled in triplicate from each sack. The herbs used were: anise (*P. anisum* I), fennel (*F. vulgare*), star anise (*Illicum verum*), coriandrum (*Coriandrum sativum* L), mastic (*Pistacia lentiscus Chia*), cardamom (*Elettaria cardamomum*), nutmeg (*Myristika fragrans*), cinnamon (*Cinnamomum*) and barley (*Hordeum vulgare*).

2.2. Production process emulation

The samples from the aromatic herbs were distilled in a 20 l bronze pilot pot still and a typical glass still using a 0.5 l Pyrex boiler, with the addition of 50% deionized water–ethyl alcohol (WA) solution. The ethyl alcohol used was derived from molasses and its metal content was far below atomic absorption spectrophotometry (AAS) detection limits.

In the pilot pot still, an actual pot still miniature, 1 kg of aromatic herbs with 4 l of 50% WA solution was distilled. For the glass still, 1/20 of the herbs mass and WA solution volume was used. The end of the distillation was noted when the residue was 1/4 of the initial WA solution volume. Sample from the residue was obtained and designated for further analysis.

2.3. Analysis

Using an Schott-Gerate pH-meter CG 818 (pH $\pm$ 0.01), the pH of every sample was measured. Turbidity, suspended and total solids, BOD, Cl^-, SO_4^{2-}, K^+, Na^+ and Ca^{2+} measurements were made only for waste samples. Results are shown in Table 1.

For the metals analysis, 150 ml of each sample were dried at 95 °C, and concentrated nitric acid was added and the mixture heated until the sample was fully digested.

All samples were assayed for Cu, Zn, Ni, Cr, Cd and Fe using a Perkin-Elmer Atomic Absorption Spectrometer 3300 PC. All analyses were run in triplicate and mean values are reported. Results for the waste are shown in Table 2 and for the herbs in Tables 3 and 4.

A SEM micrograph of the content of the waste was made using back-scattered electron image and WDXA, both at 25 KV and magnification 360×, with a JEOL JSM-35CF.

Table 1
Physicochemical characteristics of the distillation process waste

pH	4.1–5.1
Turbidity (NTU)	28–38
Suspended solids (%)	0.35–0.45
Total solids (%)	2.0–2.4
Concentration (mg/l)	
Cl^-	485–615
SO_4^{2-}	3.1–4.1
K	1480–1780
Na	595–745
Ca	285–345

Table 2
Range of metals concentration in the waste

Type of Metal	Concentration range (mg/l)
Fe	60.25–157.50
Cu	53.75–82.50
Ni	0.41–8.36
Zn	3.15–31.25
Cd	0.06–1.36
Cr	0.08–1.05

Table 3
Analysis of the residue from glass still

Sample	pH		Metals concentration (mg/l)					
	Day	Month	Fe	Cu	Zn	Ni	Cr	Cd
Aniseed	5.72	5.50	7.05	1.02	2.62	0.88	<0.01[a]	0.02
Star anise	3.80	4.12	3.51	0.29	0.81	0.27	<0.01	0.07
Fennel	6.08	6.17	7.30	1.00	6.60	1.17	<0.01	0.12
Barley	6.58	4.30	2.28	0.22	3.27	0.02	<0.01	0.08
Coriandrum	5.76	5.88	3.03	1.57	4.87	0.46	<0.01	0.07
Cinnamon	4.98	4.74	1.37	0.26	2.27	0.15	0.05	0.03
Cardamom	4.07	4.32	8.87	1.48	4.87	0.43	<0.01	0.06
Nutmeg	5.25	5.73	3.30	0.83	1.47	0.49	<0.01	<0.01
Mastic	4.36	5.10	1.58	0.10	0.17	0.13	<0.01	0.01

[a] It is below AAS detection limit (0.01 mg/l).

Furthermore, a 10 ml sample from aniseed, fennel and star anise residues resulting from a glass still, were subjected to HPLC separation using a Hewlett-Packard 1050 HPLC device with a UV Diode Array Detector 110 at 265, 280, 316, 320 and 365 nm. The column used was an Spherisorb ODS2 250 mm × 4 mm (∅ 5 μm) and the solvents A: methanol, B: water–$HClO_4$ with a gradient washing system for 95 min. The samples were diluted 1:10

Table 4
Analysis of the residue from bronze pot still

Sample	pH		Metals concentration (mg/l)					
	Day	Month	Fe	Cu	Zn	Ni	Cr	Cd
Aniseed	5.62	5.58	8.55	5.73	4.98	1.14	0.02	0.08
Star Anise	4.34	4.57	5.51	3.69	4.71	0.83	<0.01[a]	0.09
Fennel	5.68	5.55	8.64	4.04	8.85	1.50	0.02	0.14
Barley	5.95	5.24	3.25	3.57	4.75	0.32	0.03	0.09
Coriandrum	6.44	6.51	4.72	4.60	6.10	0.82	0.04	0.07
Cinnamon	5.00	4.91	2.26	2.12	3.74	0.37	0.05	0.03
Cardamom	5.52	5.60	10.63	7.00	10.57	0.88	0.02	0.07
Nutmeg	5.02	5.22	4.46	3.15	2.85	0.82	0.01	0.02
Mastic	3.89	3.99	2.87	2.44	1.61	0.57	0.03	0.02

[a] It is below AAS detection limit (0.01 mg/l).

using 50% WA solution. Special care was provided to avoid samples contamination with metals. Fifteen milligram per litre of Cu, Ni and Zn were added to 10 ml glass still residues and lead to HPLC.

3. Results and discussion

3.1. Waste description

The waste tested in this work was acidic, aqueous industrial waste of intense smell, formed during the fermentation and after the distillation process. Since there were 12 samples of the waste, taken at a different production dates/times, there was a range of metal concentration values and physicochemical characteristics reported. This can be assumed as typical of systems using natural ingredients as raw materials.

3.2. Aromatic herbs

The herbs used for flavoring the spirit can contain many WA extractable metals, for each type of distillation, i.e. glass still and bronze pot still, respectively (Tables 3 and 4).

Heavy metals, such as Ni, Zn, Cr and Cu were mainly of interest. Free disposal of waste containing such metals is prohibitive for environmental purposes. The concentration of Fe is important in respect to the waste color, which may be a limiting agent to waste disposal.

pH was measured 1 day after the sample was taken and 1 month after distillation took place. No significant changes are reported, as it is evident (Tables 3 and 4), that storing samples for a short period of time does not influence the results. Very low BOD values further supports this conclusion. The pH is in the acidic region, from 3.8 (star anise residue) to 6.2 (fennel residue).

3.3. Determining the metal content sources

Comparing the data for aniseed from Tables 3 and 4 illuminates on the main source of metal content in the waste; the pot stills. More acidic residues cause an increased pot still corrosion, as it is evident in star anise results.

Table 5
Statistical terms (ANOVA method: two independent factors for metals concentration)

Metal	Factor: herb type			Factor: pot still type		
	F	*P*-value	*F*-criterion	*F*	*P*-value	*F*-criterion
Cu	2.958	0.073	3.438	70.508	3.08×10^{-5}	5.318
Fe	235.201	1.11×10^{-8}	3.438	128.058	3.35×10^{-6}	5.318
Ni	48.089	5.74×10^{-6}	3.438	104.917	7.09×10^{-6}	5.318
Zn	9.956	0.0019	3.438	21.984	0.0015	5.318

Table 6
Analysis of variation of two non-co-related factors (parameter: Cu concentration mg/l)[a]

Conclusion	Data number	Sum (mg/l)	Mean value (mg/l)	Variation		
1	2	6.75	3.375	11.092		
2	2	3.98	1.99	5.78		
3	2	5.04	2.52	4.62		
4	2	3.79	1.895	5.611		
5	2	6.17	3.085	4.59		
6	2	2.38	1.19	1.729		
7	2	8.48	4.24	15.235		
8	2	3.98	1.99	2.691		
9	2	2.54	1.27	2.737		
1	9	6.77	0.752	0.313		
2	9	36.34	4.038	2.414		
Source of variation	SS	FN	MS	*F*	*P*-value	*F*-criterion
Analysis of variation						
Lines	16.304	8	2.038	2.958	0.073	3.438
Rows	48.577	1	48.577	70.508	3.08×10^{-5}	5.318
Error	5.512	8	0.689			
Sum	70.393	17				

[a] Cu concentrations as shown in Tables 3 and 4.

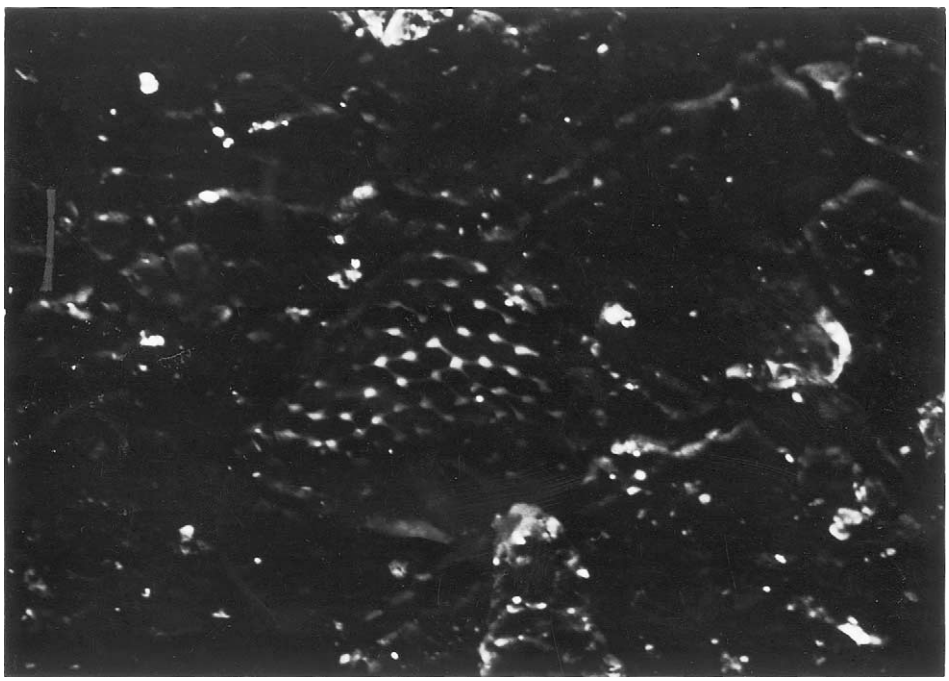

Fig. 1. Waste content from the distillation process, SEM micrograph (360×).

A glass still contains no metals in its materials of construction. Most metal concentrations in Table 3 were >0.01 mg/l (for Fe, Cu, Ni and Zn), which is considered a high level. It has been determined that metal content in plants comes from pesticide and/or fertilizer use [10–13].

Bronze contains several metals besides its basic constituents Cu and Zn, such as Ni, Sn and Fe, depending on the alloy used. Traces of Cd and Cr were found in the sack containing the herbs during distillation.

The impact of the kind of herb and type of distillation equipment on metals concentration can be determined using the analysis of variation (ANOVA) method at an importance level of $a = 0.05$ [14]. Table 5 indicates that Cu concentration is clearly adjusted by the pot still type, not the type of herb. For all other metals (Fe, Ni and Zn) both factors are of importance. Cd and Cr have a lot of indefinable concentrations (<0.01 mg/l) and cannot give solid results. Table 6 shows the ANOVA method for Cu. However, the involvement of the raw materials cannot be determined with accuracy. This result is mainly due to the following:

1. The exact synthesis (“recipe”) of the aromatic herbs used is not publicly available (i.e. it is producer patented information).
2. Likewise for every “recipe” there is a different affect on the pot stills, due to pH changes, extracted organic compounds varying concentration, etc. and there are no exact methods of predicting the raw material effect in metal accumulation.

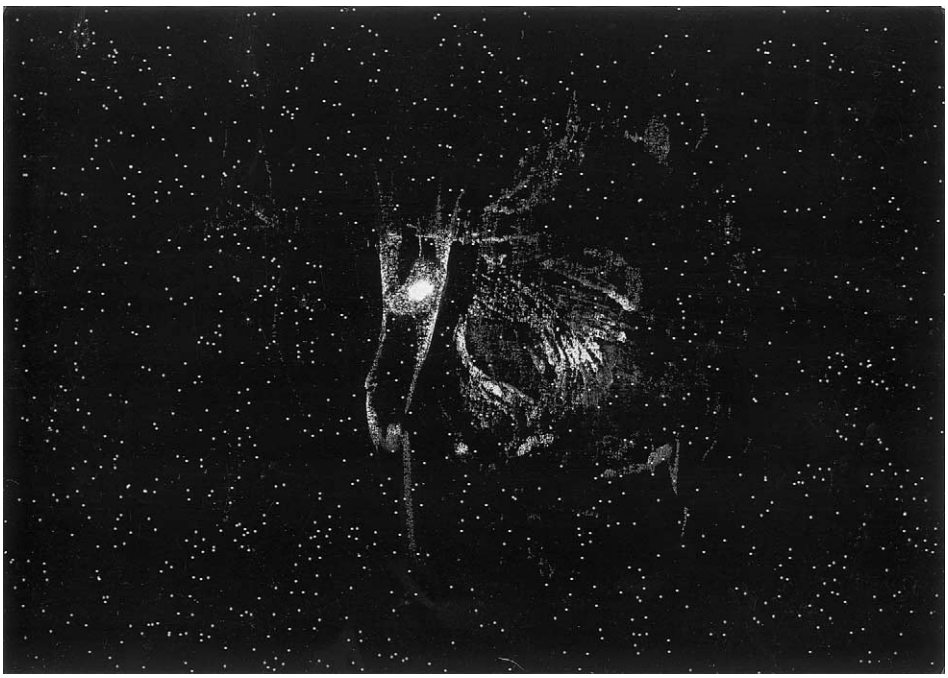

Fig. 2. Copper WDXA of the SEM micrograph (360×).

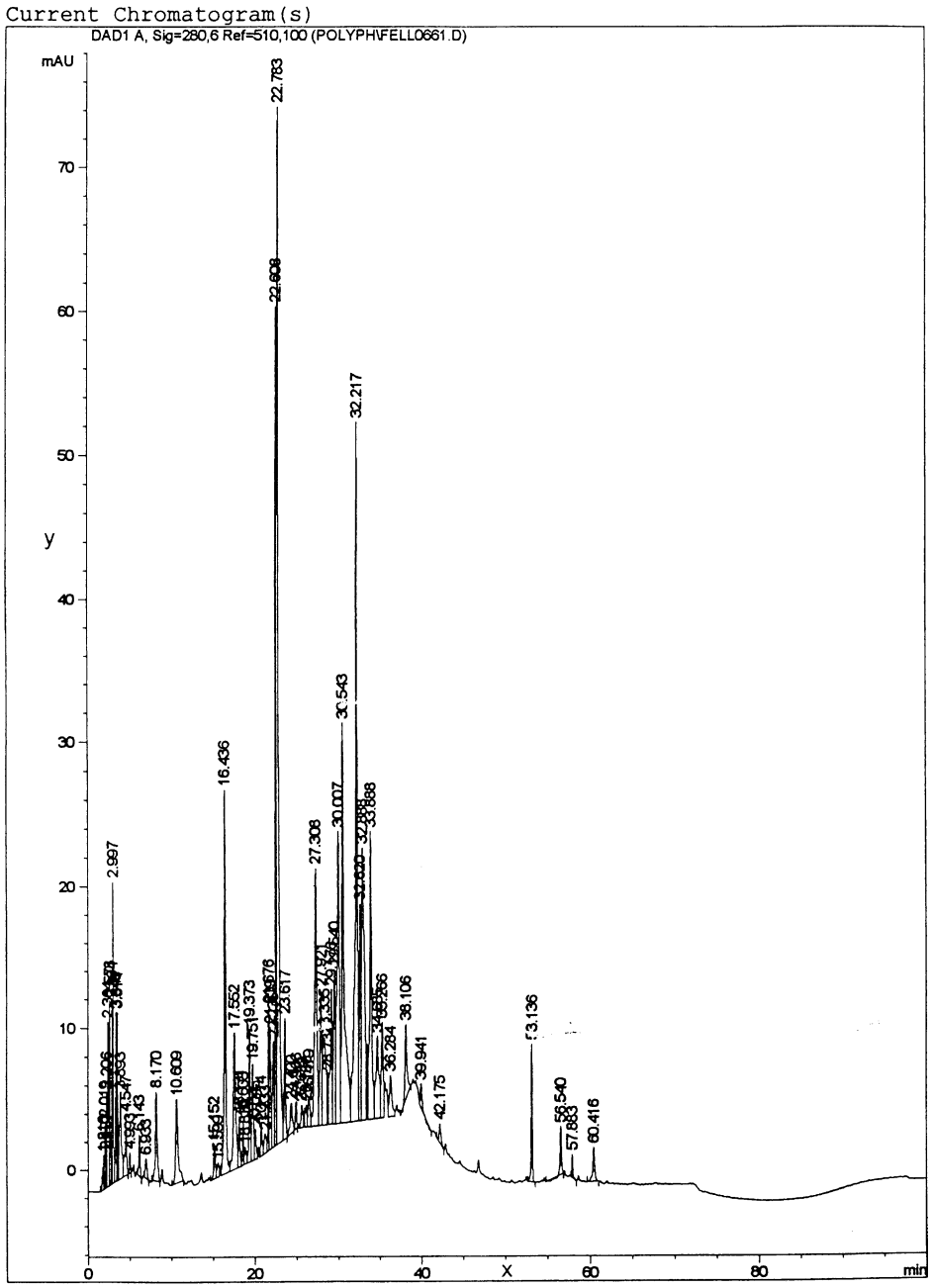

Fig. 3. Chromatogram of aniseed residue from glass still (280 nm).

3.4. Formation of complexes

The alloy, the pot still is made of, is important to the spirit flavor (bouquet). The flavor is considered to be protected by complex formations that retain heavy or odorous substances [1]. Bronze, distillers experience indicate, has proved to be one of the best metal alloys for this purpose. Cu, Zn, Ni and Fe complexes are mainly of interest, because of their concentrations in the waste; these metals are provided by the corrosion of the pot stills and react with organic substances extracted from the herbs during distillation.

Metals existence was verified by SEM micrograph (Figs. 1 and 2). Fig. 1 shows the solid content of the waste after evaporation to dryness, and Fig. 2 is the corresponding image with WDXA applied for copper. The existence of Cu in the amorphous phase, supports the formation of metal–organic complexes. In general, large molecules are formed, as it was detected by HPLC. The use of complexation data will be particularly useful to waste treatment, i.e. treatment process, temperature, pH and other parameters [15]. Methods that use fly ash, or sawdust for the retention of metals from such wastes have been studied by Moutsatsou et al. [2,9].

Complex compound formation is obvious in HPLC separations (Figs. 3–5). Each wavelength corresponds to a range of organic compounds:

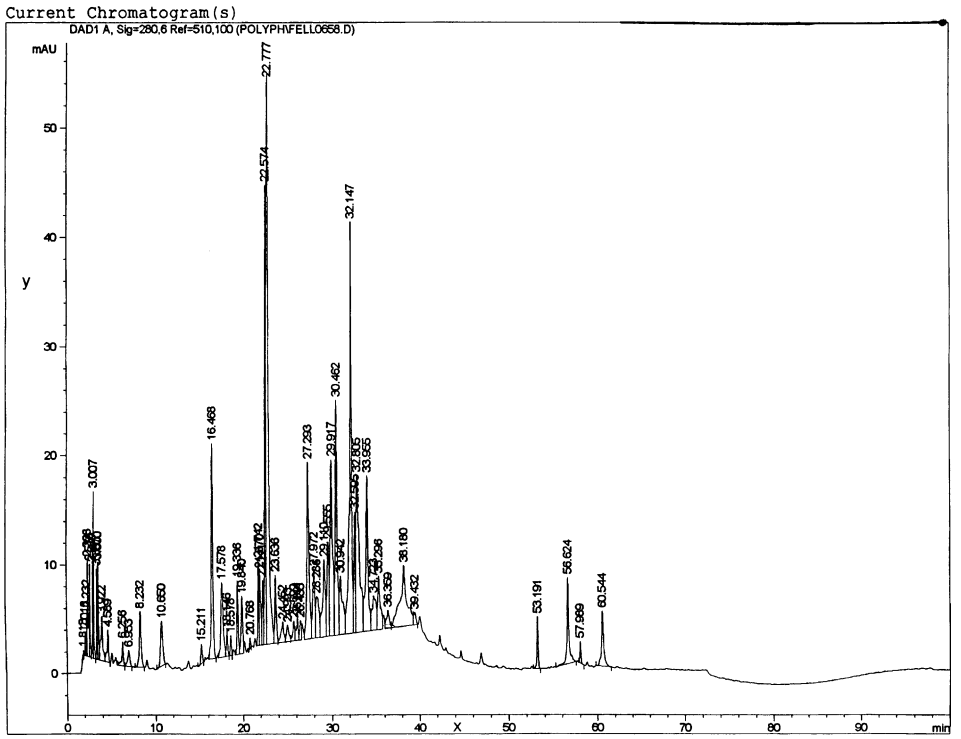

Fig. 4. Chromatogram of aniseed residue from glass still with 15 mg/l Cu added (280 nm).

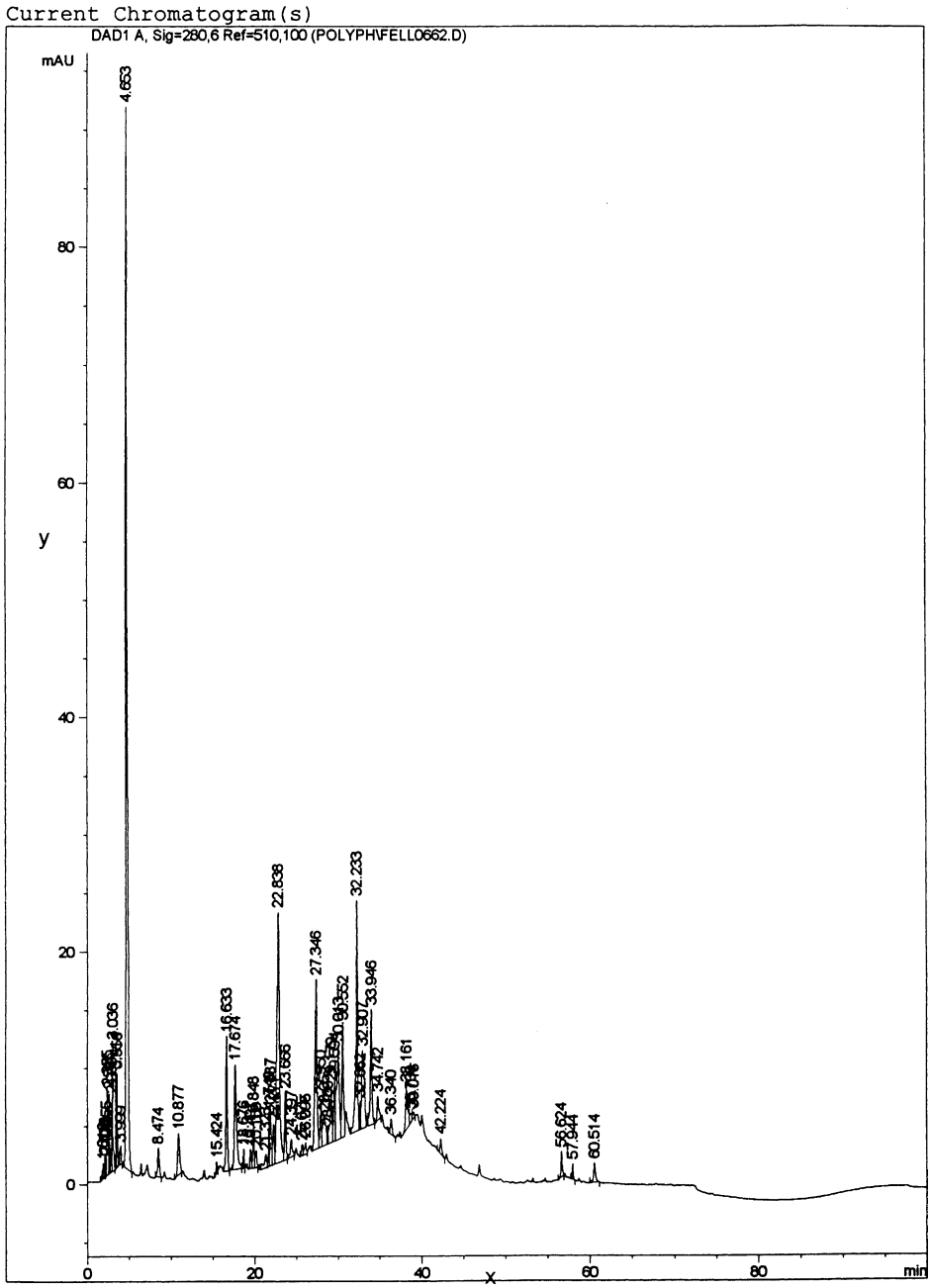

Fig. 5. Chromatogram of aniseed residue from glass still with 15 mg/l Ni and Zn added (280 nm).

- 265 nm for a part of flavons and flavanols;
- 280 nm for flavanols-3 up to catechin (flavapentol) and the products of benzoic acid;
- 316 nm for hydroxy-cinnamonic acids up to caffeic acid;
- 320 nm for *p*-coumarate;
- 365 nm for the rest of flavons and flavanols up to rutin.

Due to the presence of numerous organic compounds and qualitative approach of complexation the type of each complex by HPLC characterization was not pursued.

These diagrams show glass still aniseed residue (Fig. 3) and residue with added copper (Fig. 4), nickel and zinc (Fig. 5), respectively for 280 nm. Metals were added in order to estimate their influence on chromatogram peaks. Only 280 nm aniseed residue chromatograms are displayed herein as most representative. All other wavelengths verified that the herbs residues show similar behavior. Aniseed residue was selected because in the distillation of anis-type beverages more than 50% of the herbs mass is aniseed or fennel.

In the chromatograms, axis *x* represents time in minutes and axis *y* represents absorption units in mAU. Using data taken from the chromatograms for 280 nm we can see, e.g. peaks #1 and #2 for 1.816 and 2.019 min with surface areas of 23.77 and 43.41 mAU s, respectively, (Fig. 3). For the same peaks, as shown by UV spectra, appearing at 1.813 and 2.018 min when Cu was added, there was great attenuation to 1.87 and 9.37 mAU s (Fig. 4). Residue with Ni and Zn added shows similar results with 10.76 and 14.69 mAU s for 1.816 and 2.035 min (Fig. 5).

It is obvious that the metal addition decreases or increases the number of peaks, their height and surface that appear at approximately the same time. This result happens mainly because new ingredients are formed (i.e. complexes of metals with organic compounds) or already formed complexes concentration increases after the addition.

4. Conclusions

The presence of heavy metals in the waste of anis-type alcoholic drink production lead to the study of the residues of the raw materials used for flavoring. Experiments showed that the metal content comes mainly from the distillation equipment used in the production and to a much lesser degree from the herbs. Metal content in the residues is attributed mainly to pot stills corrosion from organic compounds extracted from the herbs with WA solution. A large number of compounds in the residue is available for complexation, as shown by HPLC. The use of SEM with WDXA further supports complexes formation, which are considered to protect the spirit flavor and explain traditional use of bronze pot stills, even for other types of distilled beverages, a new finding in the field of distilled beverages. The forming of large molecules favors precipitation and/or chemi-sorption treatment methods.

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