Analysis of trace elements in Turkish raki by differential pulse polarography

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Raki is a traditional Turkish drink. It is obtained by distillation process after suma (alcoholic water) obtained from raisins is sweetened with anise (pinpinella anisum). The quality of raki depends on the quality of the grapes used in the production process and technological differences. In this study, in order to ensure consumer food safety, 10 different raki samples in Turkey were thawed by microwave cracking system, and their trace element content was examined. Differential pulse polarography (DPP), which has high selectivity and sensitivity, was used for the measurements. Appropriate measurement conditions were determined for each element. Validation of the method was done with a known sample. The detection limit of the method was determined as 0.1 μgg^{-1}. The amounts of Fe, Cu, Pb, Cd, Cr, As, Ni, Zn, Se elements in the raki samples were determined as approximately 2-80 μgg^{-1}.

1. INTRODUCTION

Raki is an alcoholic beverage obtained by distillation of suma produced in Turkey with anise, according to the Turkish Food Codex Communique on Distilled Alcoholic Beverages [1]. It is a traditional drink that is consumed quite a lot in Turkey. The use of different grape varieties and regional differences affect the quality of raki. Elemental analyzes of raki have also become extremely important.

Trace elements, which play an important role in vital functions, are obtained from foods and beverages. Analysis of trace elements in alcoholic beverages is also carried out. The consumption of alcoholic beverages in Turkey is gradually increasing. Excessive amounts of these elements can have a toxic effect and pose a significant risk to human health.

Trace element analysis in beer from alcoholic beverages, atomic absorption spectroscopy (AAS) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3-5], X-ray fluorescence spectroscopy [6-9] and polarography methods [10-11] were used. Trace elements in wine, another widely consumed

alcoholic beverage, were determined by AAS [12-13], ICP [14-21] and polarography methods [22-24]. Elemental analyzes and risk effects on health were examined using these analysis methods.

In this study, we did not encounter a study on trace element analyzes in Raki, which is widely consumed in Turkey. Elemental analyzes of 10 different raki sold in markets in Turkey were made. Here, we used differential pulse polarography method, which has high selectivity, high reproducibility, cheaper and easier to analyze compared to other spectroscopic methods.

2. EXPERIMENTAL

2.1. Material and Reagents:

The reagents (Merck) used in the measurements were weighed from metal salts of analytical purity in certain proportions and their solutions were completed with distilled water. Dilute solutions were prepared daily. Various supporting electrolytes including K_2CO_3, NH_3– NH_4Cl buffer, and HAc–NaAc buffer with or without EDTA were used over a wide pH range.

2.2. Instruments:

Entek brand polarography analyzer was used for the measurements. In this device, there are dripping mercury electrode, saturated calomel electrode, Pt wire electrode and C4 cell stand. In addition, 99.999% nitrogen gas was used to remove dissolved oxygen.

2.3. Preparation of raki samples:

The same thawing procedure was applied for ten different raki samples bought from the market. 750ml of raki sample was evaporated to a volume of approximately 10mL. 8mL HNO_3 and 2ml $HClO_4$ were added to the samples taken to A flask with long neck (30cm), evaporated. This process was repeated 4 times. The volume of the clear sample was made up to 10 mL with distilled water.

3. RESULT AND DISCUSSION

3.1. Preliminary Experiments:

Elements have specific peak potentials in certain buffers and electrolytes. These buffers and electrolytes prevent them from interfering with other elements and make quantification analyzes sensitive [25-27]. This peak potential varies depending on both the electrolytes and the pH value. The most suitable environment is determined by analyzing different electrolytes and pH values with polarography.

Potentials suitable for determination of elements in raki samples were examined. Potential values depend on the type of electrolyte and its pH values. The potentials where the peaks of each element

diverged and the sensitivity was the highest were determined and given in Table 1. According to these data, pH=7.0 Hac+EDTA for Fe, pH= 11.0 1 M K_2CO_3 for Cu, pH= 11.0 1 M K_2CO_3 for Pb, pH= 9.8 NH_3/NH_4Cl buffer for Ni and Zn, pH 1.0-4.0 Vol electrolyte for As (III) and Se (IV) were analyzed.

Table 1. Effect of electrolytes and pH on peak potentials (V) of some elements in the presence of digested raki (V vs. SCE)

	pH 3.5 (1M Hac)	pH 7 (1 M Hac+ 0.1 M EDTA)	pH 10 (1 M NH₃-NH₄Cl)	pH 11 (1M K₂CO₃)
Fe (III)	-0.05	-0.17	-0.32	-0.00
Cu (II)	-0.12	-0.00	-0.38	-0.27
Pb (II)	-0.40	-0.54	----	-0.58
Ni (II)	----	-0.90	-0.95	-0.79
Zn (II)	-0.96	-1.15	-1.25	-1.00
As (III)	----	----	----	----
Se (IV)	-0.54	----	----	----

Using these results, qualitative and quantitative analysis of the elements in the raki samples was made. The results obtained are summarized in Table 2.

Table 2. Trace element amounts ($\bar{x} \pm ts / \sqrt{N}$) (μgL^{-1}) in 10 different digested raki samples. (V vs. SCE). CI 95%, N=4. $\bar{x}$: Arithmetic mean, s: Standard deviation, t: Student's t-test

Element	Fe³⁺	Cu²⁺	Pb²⁺	Ni²⁺	Zn²⁺	As³⁺	Se⁴⁺
Sample 1	21 ± 2	14 ± 1	15 ± 1	27 ± 2	34 ± 3	3 ± 0.1	58 ± 5
Sample 2	23 ± 2	13 ± 1	18 ± 1	29 ± 2	33 ± 3	3 ± 0.1	63 ± 5
Sample 3	24 ± 2	16 ± 1	17 ± 1	28 ± 2	35 ± 3	3 ± 0.1	66 ± 6
Sample 4	25 ± 2	16 ± 1	17 ± 1	30 ± 2	35 ± 3	4 ± 0.1	70 ± 6

Sample 5	25 ± 2	14 ± 1	16 ± 1	32 ± 2	37 ± 3	4 ± 0.1	74 ± 6
Sample 6	27 ± 2	18 ± 1	19 ± 1	33 ± 2	38 ± 3	5 ± 0.1	74 ± 6
Sample 7	27 ± 2	19 ± 1	19 ± 1	34 ± 2	39 ± 3	5 ± 0.1	76 ± 7
Sample 8	29 ± 2	19 ± 1	18 ± 1	34 ± 2	39 ± 3	5 ± 0.1	76 ± 7
Sample 9	28 ± 2	13 ± 1	16 ± 1	29 ± 2	37 ± 3	4 ± 0.1	65 ± 6
Sample 10	26 ± 2	15 ± 1	15 ± 1	28 ± 2	34 ± 3	3 ± 0.1	56 ± 5

3.2. Fe (III):

The most suitable medium for separating iron (III) peak from copper is pH=7.0 HAc-Ac electrolyte in the presence of EDTA. The most suitable medium for separating iron (III) peak from copper is pH=7.0 HAc-Ac electrolyte in the presence of EDTA and it is given in figure 1. The amount of Fe (III) was determined by standard additions. The amount of Fe (III) in ten different raki samples was measured as 20 to 30 mgL^{-1} as the 95% confidence level and the average of 4 measurements.
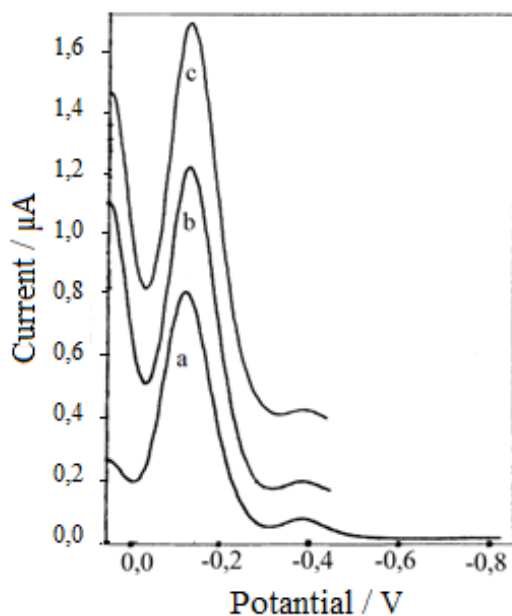

Figure 1. Differential pulse polarographic determination of iron in Turkish raki samples. A) 9 mL 1 M HAc + 0.5 mL 0.5 M EDTA + 0.5 mL sample, b) + 0.2 mL 1×10^{-3} M Fe^{3+}, c) + 0.2 mL 1×10^{-3} M Fe^{3+}

3.3. Cu (II):

The most suitable medium for copper peak is 1 M K_2CO_3 (pH=11.0) electrolyte and its given

figure 2. The amount of Cu (II) in the raki samples was determined as 10 to 20 mgL^{-1} as the 95% confidence level and the average of 4 measurements.
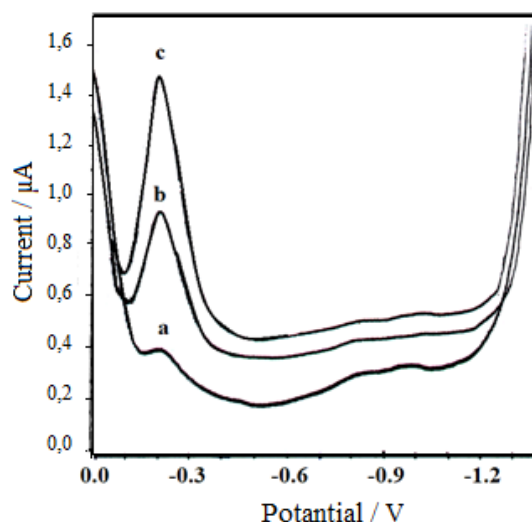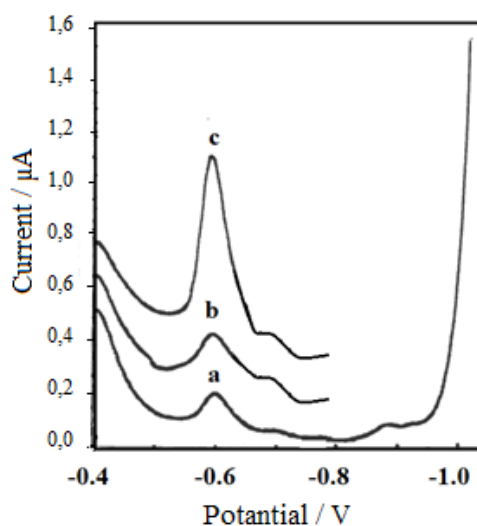

Figure 2. Differential pulse polarographic determination of copper in Turkish raki samples. A) 9.5 mL 1M K_2CO_3 + 0.5 mL sample, b) + 0.2 mL 1x10^{-3} M Cu^{2+}, c) + 0.2 mL 1x10^{-3} M Cu $^{2+}$

3.4. Pb (II):

Many metals such as Pb, As and Cd are known to have toxic effects. They can damage many vital functions. Their analysis is also important [28-29]. The most suitable medium for lead peak is 1 M K_2CO_3 (pH=11.0) electrolyte and its given figure 3. The amount of lead (II) in the raki samples was determined as 15 to 20 mgL^{-1} as the 95% confidence level and the average of 4 measurements.

Figure 3. Differential pulse polarographic determination of lead in Turkish raki samples. A) 9.5 mL 1 M K_2CO_3 + 0.5 mL sample, b) + 0.2 mL 1x10^{-3} Pb^{2+}, c) + 0.2 mL 1x10^{-3} Pb^{2+}

3.5. As (III):

As (III) is determined in HCl and HAc electrolytes at pH=1.0 to 4.0. The peak here is short and broad. It is more suitable to determine with the catalytic hydrogen peak where the sensitivity is high [30-32]. pH=3.5 0.1 M HAc electrolyte was used. No peak was observed after the polarogram of the Raki sample was taken. However, approximately 100 times as much molybdenum solution was added to the cell, and when the polarogram was taken, the catalytic hydrogen peak of As (III) was observed at -1.1 V and it was given figure 4. By adding standard solution to it, the amount of As (III) in the raki 95% confidence level and the average of 4 measurements was measured as 2 to 6 mgL^{-1}.
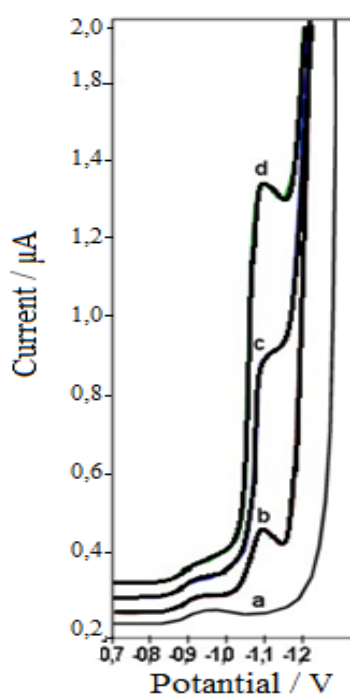

Figure 4. Differential pulse polarographic determination of arsenic in Turkish raki samples. A) 9.5 mL 1M HAc + 0.5 mL sample, b) + 1.0 mL 1×10^{-5} M Mo^{6+}, c) + 0.2 mL 1×10^{-8} M As^{3+}, d) + 0.2 mL 1×10^{-8} M As^{3+}

3.6. Ni (II):

The nickel peak is determined in pH=9.8 NH_3-NH_4Cl buffer. The nickel peak is seen in figure 5 at -0.95 V. The amount of nickel (II) in the raki samples was determined as 25 to 35 mgL^{-1} as the 95% confidence level and the average of 4 measurements.
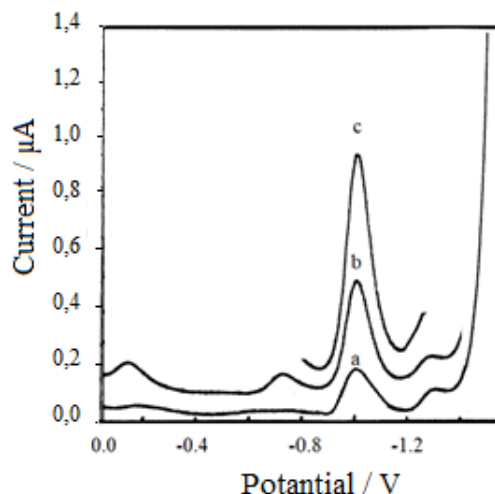
Figure 5. Differential pulse polarographic determination of nickel in Turkish raki samples. A) 9.5 mL NH$_3$-NH$_4$Cl buffer + 0.5 mL sample, b) + 0.2 mL 1x10^{-3} M Ni^{2+}, c) + 0.2 mL 1x10^{-3} M Ni^{2+}

3.7. Zn (II):

The zinc peak is determined in pH=9.8 NH$_3$-NH$_4$Cl buffer. The zinc peak is seen in figure 6 at -1.25 V. The amount of zinc (II) in the raki samples was determined as 30 to 40 mgL^{-1} as the 95% confidence level and the average of 4 measurements.
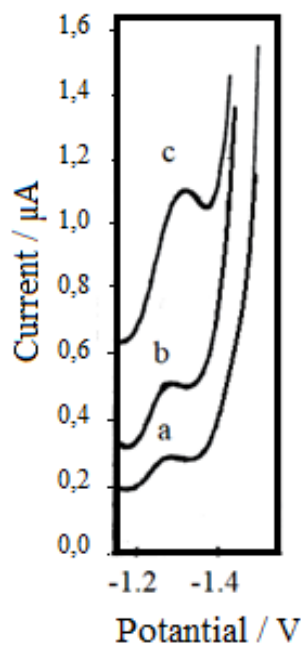

Figure 6. Differential pulse polarographic determination of zinc in Turkish raki samples. A) 9.5 mL NH$_3$-NH$_4$Cl buffer + 0.5 mL sample, b) + 0.2 mL 1x10^{-3}M Zn^{2+}, c) + 0.2 mL 1x10^{-3}M Zn^{2+}

3.8. Se (IV):

In real samples, Se (IV) cannot be determined easily due to the interference effect. Catalytic hydrogen peak was used for Se (IV) determination. In the pH=3.5 1M HAc electrolyte, a catalytic hydrogen peak was observed with molybdenum at approximately -1.0 V in figure 7. By adding standard solution on it, the amount of Se (IV) in the raki samples was determined as 95% confidence level and 50 to 80 mgL^{-1} as the average of 4 measurements.
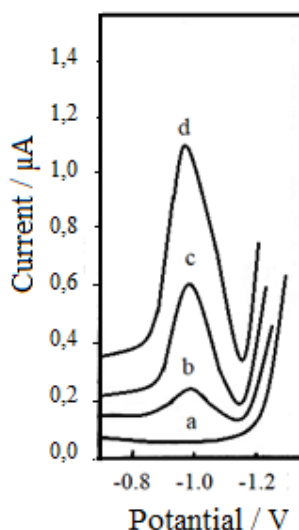

Figure 7. Differential pulse polarographic determination of selenium in Turkish raki samples. A) 9.5 mL 1M HAc + 0.5 mL sample, b) + 1.0 mL 1x10^{-5} M Mo^{6+}, c) + 0.2 mL 1x10^{-8} M Se^{4+}, d) + 0.2 mL 1x10^{-8} M Se^{4+}

3.9. Comparison of results with AAS:

To compare the method, trace elements in the raki sample were measured by atomic absorption spectroscopy and the % recovery results are given in Table 3. The results were found to be compatible with both methods.

Table 3.   Comparison of trace elements amounts ($\bar{x} \pm ts / \sqrt{N}$) (µg/L) in Sample 1 with AAS. (CI 95%, N=4. $\bar{x}$: Arithmetic mean, s: Standard deviation, t: Student's t-test)

Element	DPP	AAS	% Recovery
Fe^{3+}	21 ± 2	20 ± 2	95
Cu^{2+}	14 ± 1	13 ± 1	93

Pb^{2+}	15 ± 1	14 ± 1	93
Ni^{2+}	27 ± 2	26 ± 2	96
Zn^{2+}	34 ± 3	34 ± 3	100
As^{3+}	3.0 ± 0.1	2.9 ± 0.1	97
Se^{4+}	58 ± 5	56 ± 5	97

4. CONCLUSION

Trace element analysis was done in raki and this was the first study. Trace amounts of Fe (III), Cu (II), Pb (II), Ni (II), Zn (II), As (III) and Se (IV) in 10 different raki samples widely consumed in Turkey, good selectivity, low the detection limit and high reproducibility were determined by differential pulse polarography. Appropriate determination conditions were determined for each element by using different buffers and electrolytes. This increases the sensitivity of the method. Differential pulse polarography method does not have problems such as interference effect, concentration of samples and taking a long time for analysis seen in other methods. These elements take place in the vital functions of people and have important duties. Pb (II) and As (III) elements, which have toxic effects, were also measured, but it was determined that there was no amount that would put human health at risk.

References

1. Turkish Food Codex Communiqué on Distilled Alcoholic Beverages (Communiqué No: 2016/55), No: 30014.
2. C. C. Nascentes, M.Y. Kamogawa, K.G. Fernandes, M.A.Z. Arruda, A.R.A. Nogueira, J.A. No´ bregaa, *Spectrachimica Acta Part B*, 60 (2005) 749.
3. A. Asfaw and G. Wibetoe, *Microchimica Acta*, 152 (2005) 61.
4. N. Mahmood, N. Petraco, Y. He, *Anal Bioanal. Chem.,* 402 (2012) 861.
5. L. Alexa, A. Kántor, B. Kovács, N. Czipa, *J. Microbiol Biotech Food Sci.*, 7 (4) (2018) 432.
6. R. Dalipi, L. Borgese, A. Zacco, K. Tsuji, E. Sangiorgi, R. Piro, E. Bontempi, L.E. Depero, *International Journal of Environmental Analytical Chemistry*, 95 (13) (2015) 1208.
7. E.M. Gama, C.C. Nascentes, R.P. Matos, G.C. Rodrigues, G.D. Rodrigues, *Talanta*, 174 (2017) 274.
8. H. Sahraoui, M. Hachicha, *J. Fundemental and Applied Sciences*, 9 (1) (2017) 468.
9. G. Siviero, A. Cinosi, D. Monticelli, L. Seralessandri, *Spectrochimica Acta*, 144 (2018) 15.
10. G. Somer, Z. Almas, *Journal of Electroanalytical Chemistry*, 593 (2006) 179.
11. G. Somer, Ş. Kalayci, *Canadian of Journal Chemistry*, 92 (2014) 221.

Int. J. Electrochem. Sci., 16 **(2021)** Article ID: 210932

10

12. S. Galani-Nikolakaki, N. Kallithrakas-Kontos, A.A. Katsanoa, *The Science of the Total Environment*, 285 (2002) 155.
13. S. Santos, N. Lapa, A. Alves, J. Morais, B. Mendes, *Journal of Environmental Science and Health, Part B* 48 (2013) 364.
14. G. Thiel, G. Geisler, I. Blechschmidt, K. Danze, *Anal. Bioanal. Chem.*, 378 (2004) 1630.
15. Ž. Fiket, N. Mikac, G. Kniewald, *Atomic Spectroscopy*, 31 (1) (2010) 44.
16. Ž. Fiket, N. Mikac, G. Kniewald, *Food Chemistry*, 126 (2011) 941.
17. M.J. Cabrita, N. Martins, P. Barrulas, R. Garcia, C. B. Dias, E.P. Perez-Alvarez, A.M.C. Freitas, T. Garde-Cerdan, *Food Control*, 92 (2018) 80.
18. Z. Deng, A. Zhang, Z. Yang, Y. Zhong, J. Mu, F. Wang, Y. Liu, J. Zhang, Y. Fang, *Molecules*, 24 (2019) 248.
19. A.A. Khalafyana, Z.A. Temerdasheva, A. A. Kaunovaa, A.G. Abakumova, V.O. Titarenkoa, V.A. Akin'shinaa, E.A. Ivanovets, *Journal of Analytical Chemistry*, 74 (6) (2019) 617.
20. E.P. Pérez-Álvareza, R. Garciab, P. Barrulasd, C. Diasd, M.J. Cabritae, T. Garde-Cerdána, *Food Chemistry*, 270 (2019) 273.
21. L. Fu, S. Shi, *Food Chemistry*, 299 (30) (2019) 125172.
22. P. Dostalek, R. Koplik, M. Patzak, *Crezh J. Food Sci.*, 17 (2) (1999) 73.
23. G. Somer, A.C. Caliskan, *J. Applied Elektrochemistry*, 39 (2009) 2027.
24. G. Somer, Ş. Kalayci, Ü. Yılmaz, *Russian Journal of Electrochemisty*, 55 (12) (2019) 1360.
25. G. Somer, Ü Ünal, *Talanta*, 62 (2004), 323.
26. G. Somer, G. Özyörük, M.E. Green, *Analyst*, 110 (1985) 151.
27. G. Somer, A. Ünlü, O. Şendil, *Anal. Chem. Lett.*, 5(6) (2011) 328.
28. C. Weisel, M. Demak, S. Marcus, B.D. Goldstein, *Am. J. Public Health*, 81 (1991) 756.
29. S.R. Williams, MosbyYear Book, Inc., Missouri, (1995) p 14.
30. R. Inam, G. Somer, *Anal. Sci.*, 14 (1998) 399.
31. R. Inam, G. Somer, *Talanta*, 46 (1998) 1347.
32. G. Ekmekçi, R. Inam, G. Somer, *Anal. Sci.*, 16 (2000) 1151.