Voltammetric Determination of Lead and Copper in Wine by Modified Glassy Carbon Electrode

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This paper describes the determination of Pb and Cu with a Nafion-modified glassy carbon electrode and $MnCo_2O_4$ nanoparticles as working electrode for anodic stripping voltammetry. Pb and Cu were accumulated in HCl/KCl (0.1 mol dm^{-3}) at a potential of –1.4 V (*vs.* Ag/AgCl electrode) for 480 s, followed by a linear sweep anodic stripping voltammetry (ASV) scan from –1.0 to +0.5 V. Under optimum conditions, the calibration curves were linear in the range of 0.01 – 8 and 0.01 – 5 mg dm^{-3} for Pb and Cu, respectively. Effect of sample dilution, accumulation time and potential were optimized. A study of interfering substances was performed. A significant increase in current was obtained at the modified electrode in comparison with the bare glassy carbon electrode. The modified electrode was successfully applied for determination of Pb and Cu in wine samples after a simple preparation procedure. Pb and Cu content in wine was used for estimation of the target hazard quotient (THQ) values for minimal and maximal levels of the metals.

Keywords Nanoparticles, lead, copper, stripping voltammetry, electrode modification, wine

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Introduction

Wine presents a highly complex organic matrix consisting of various substances, such as sugars, alcohols, organic acids, aldehydes, phenols, flavonoids, lanthanides, tannins, and also some microelements. The quality and organoleptic characteristics (color, taste, and aroma) of wines depend on the presence and the amount of these substances.[1,2] Microelements such as heavy metals are often part of the wine matrix. Their primary role is to stimulate redox reactions, which are very important for the aging process of wines. Heavy metals originate from different natural sources, such as rocks, soil and water. It is considered that the highest percent of heavy metal ions in wine originates from the soil.[3,4] In the ripening phase, metal ions from soil incorporate themselves into the grapes through the root. The amount of heavy metals as well as their presence can be used for the determination of origin, variety, and type of wine and other beverages. Other sources that contribute to higher content of heavy metals in wine are environmental pollution and addition of substances for growth and disease control. Utilization of fertilizers, fungicides and pesticides during the growing season elevates the content of metal ions, such as Mn, Zn, Cu, Cd, and Pb.[5,6] The wine will probably have an increased content of Cd and Pb if the vineyard is located near roads. Increased content of heavy metals in the wine can have a harmful effect on human health so it is extremely important to monitor the content of toxic substances during wine production.[7,8]

There are many techniques that have been used for the determination of heavy metal ions in wine. The most commonly used methods are atomic absorption and emission spectroscopy, such as flame atomic absorption spectroscopy (FAAS),[9–12] inductively coupled plasma optical emission spectroscopy (ICPOES),[13,14] and inductively coupled plasma mass spectroscopy (ICPMS).[13,15,16] However, these well-known methods require expensive instruments and long operating time, the latter of which is not suitable for the analyses of a large number of samples. Electrochemical methods, including stripping chronopotentiometry, stripping voltammetry,[17] and stripping potentiometry have been applied successfully for the determination of heavy metals[18] and organic substances.[19] The sensitivity, selectivity, low-cost and simple equipment, and possibility for simultaneous determination of metal ions are some advantages of electrochemical methods.[1,20,21] Mercury film, mercury drop and amalgam electrode were previously used for metal ions determination but taking into consideration the harmful environmental impact of mercury based electrodes,

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they were replaced with some alternative electrode materials such as carbon based electrodes. The most serious problem for determination of metal ions in wine by stripping voltammetry is interference of some organic substances in wine, which results in formation of an inert complex. Formation of such a complex contributes to weakening measurement sensitivity due to complex adsorption on the electrode surface. The layer formed on the surface of the electrode can change the kinetics of the electrode reaction, affecting the rate of diffusion of analyte ions.[20] To overcome this problem, some authors have suggested different methods related to the pretreatment process of wine samples. Generally, it is very rarely possible to analyze any food samples without previous treatment.[22] Wet digestion in a closed system with the addition of reagents to solubilize and/or oxidise an organic compound is the most commonly used.[23] However, this pretreatment method can result in sample contamination problems, mostly due to the interaction of the investigated sample with vessels during the storage period. Moreover, any introduction of new reagents additionally increases the risk of contamination.[20,22] A very efficient method of wine pretreatment is microwave oven digestion, which offers better process control than any other heating method.[24] To avoid all these problems, some authors have suggested an electrochemical method for mineralizing wines in a four-electrode electrolyzer for voltammetric determination of Cu(II), Pb(II), and Zn(II)[20] where a glassy carbon crucible served as the working electrode. To improve selectivity and sensitivity of the electrode as an instrument for heavy metal detection, much effort has been devoted to the modification of the electrode surface with different nanomaterials. In recent years, numerous papers have reported on the utilization of variety metal oxide nanoparticles, such as Fe_3O_4,[25,26] Co_3O_4,[27] Cr_2O_3,[28] as modifiers of the electrode surface for determination of metal ions in real samples. Spinel structure metal oxides with common chemical formula AB_2O_4, where A and B are divalent and trivalent metal ions, have great potential for electrochemical applications due to their unique structural, magnetic, and electrical properties.[29-33]

The aim of this work was to develop a glassy carbon modified electrode for determination of Pb and Cu by anodic stripping voltammetry (ASV). A modified electrode was immobilized with Nafion by a simple construction procedure for determination of analytes in wine samples. The modification of the glassy carbon electrode at the microgram level in wine samples after simple sample preparation has been demonstrated and satisfying recoveries were achieved.

Experimental

Reagents and wine samples

Reagents of chemically pure grades (HCl, KCl, HNO_3, H_2O_2) were used in these experiments. Lead and copper solutions were prepared from atomic absorption spectrometry standards (1000 mg dm^{-3}, Panreac, Germany). Nafion perflurinated ion-exchange resin (5%) was purchased from Aldrich. Ultrapure water was used for all analyses. Characteristics of the wine samples are given in Table 1. Wine samples used for these experiments were commercially obtained from the local market, and one sample was obtained from a local producer.

Instrumentation

Electrochemical measurements were performed using the CHI 800C workstation (CH Instruments, USA). The three electrode system consisted of the glassy carbon electrode (CH Instruments, Model CHI104, 3 mm in diameter), a reference electrode

Table 1 The origin of wine samples

No. of sample	Wine	Country of origin	Color	Alcohol content, %
1	Domestic	Serbia	Red	—
2	Vranac	Montenegro	Red	13.3
3	Orpheline	Serbia	Red	14
4	Rose	Montenegro	Rose	13
5	Krstač	Montenegro	White	13
6	Petsina	Greece	White	11.5

Table 2 Temperature programmes for GFAAS for both analytes

Step	$T/°C$		t_{ramp}/t_{hold} (s)
	Cu	Pb	
Drying	250	250	10/20
Pyrolysis	1200	850	5/10
Atomization	2300	1800	1/3
Cleaning	2600	2100	1/3

(Ag/AgCl, CH Instruments, Model CHI111) and a platinum wire (0.5 mm) as auxiliary electrode.

A Perkin-Elmer 2380 atomic absorption spectrophotometer with electrothermal atomization unit Model HGA-400 with background correction with deuterium lamp was used for GF-AAS (graphite furnace) measurements. As a source of radiation, hollow cathode lamps were used. Copper was measured at 324.8 nm and lead at 217 nm wavelength. The argon flow rate was 220 cm^3 min^{-1}. Graphite cuvettes made of pyrollitic graphite were used. The volume of working solution was 20 μL. Working programs of the graphite furnace (GF) for investigated metals are presented in Table 2.

Preparation of working electrode

The working electrode was modified by $MnCo_2O_4$ nanoparticles. They were synthesized by citrate gel combustion technique. They were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction pattern analysis (XRD) and simultaneous thermogravimetry and differential thermal analysis (TG/DTA). The results were published in our previous manuscript.[34]

Before the modification, the GCE was polished with alumina slurry of different grain sizes (1, 0.3 and 0.05 μm, in that order, Buehler, USA). The polished electrode was rinsed with MilliQ water and ultrasonically washed in methanol–water mixture (1/1, v/v) for 30 s. The clean GCE was dried at 50°C. Suspension for modification was prepared by adding 1 mg of $MnCo_2O_4$ powder to 2 cm^3 of MilliQ water, and it was sonicated for 30 min. The 6 μL of the suspension was applied on the clean GCE and dried at 50°C and finally 3 μL of 1% Nafion (ethanolic solution) was applied on the surface and the modified electrode was air dried and ready to use. The modified electrode was denoted as $Nafion/MnCo_2O_4/GCE$.

Preparation of the wine samples for GFAAS

For organic matter decomposition, the hot mixture of HNO_3 and H_2O_2 was used.[35] A volume of 25.00 cm^3 of wine was put in a Kjeldahl flask and 5.00 cm^3 of the concentrated nitric acid was added (63%, d = 1.43 g cm^{-3}). After, 5.00 cm^3 of peroxide

was added to the mixture and it was heated until the mixture became colorless. The solution was transferred into a 50.00-cm³ volumetric flask and diluted with MilliQ water. All samples were prepared in triplicate. The wine samples were kept at 4°C between analyses.

Preparation of wine samples for electrochemical (EC) measurements

For EC measurements, sample amounts of 23.0 cm³ of wine were acidifed with concentrated HCl so the final acid concentration was 0.5 mol dm⁻³. The solutions were stirred and after 30 min the samples were filtered through 0.45 μm nylon syringe filters into 25.00 cm³ volumetric flasks. Acidified samples were kept in a refrigerator at 4°C before analysis.

Prior to the analysis, 2.00 cm³ of acidified wine sample was pipetted into a 10-cm³ volummetric flask, diluted with KCl solution (1 mol dm⁻³) and ultrapure water so that the final concentration was 0.1 mol dm⁻³ for both HCl and KCl. That solution was transferred into an electrochemical cell and firstly deaerated by a stream of nitrogen gas (99.999%) for 10 min. The working, reference and auxiliary electrodes were immersed into the cell, stirring was switched on and the desired accumulation time and potential were applied. Anodic voltammograms were recorded at a scan rate of 50 mV s⁻¹ after 10 s quiet period without stirring at the linear sweep scan from –1.0 to +0.5 V *vs*. Ag/AgCl. The concentration of metal ions was determined by the standard addition method. All samples were prepared in triplicate.

Calculation of THQ

The target hazard quotient presents the ratio between exposure and the reference dose and it is calculated by Eq. (1), where EFr is the exposure frequency (days per year); EDtot is the exposure duration (year); SFI is the food ingestion rate (grams per day), C is concentration (μg per g); RfDo is the oral reference dose (mg per kg per day; BWa is the adult body weight (kg) and ATn is the averaging time for non-carcinogens (365 days per year times number of exposure years). A THQ value below 1 means that the exposure level is lower than the reference dose, such that the daily exposure amount will not cause any negative effects during a lifetime.[36,37]

$$ \text{THQ} = \frac{\text{EFr} \times \text{EDtot} \times \text{SFI} \times C}{\text{RfDo} \times \text{BWa} \times \text{ATn}} \times 10^{-3} \qquad (1) $$

Results and Discussion

Cyclic voltammograms of the solution containing 1 mmol dm⁻³ Pb and Cu and 0.1 mol dm⁻³ hydrochloric acid and potassium-chloride are shown in Fig. 1 at the bare GCE (b) and Nafion/MnCo₂O₄/GCE (c). The resulting voltammograms show one cathodic peak at –0.48 V on the forward scan and one sharp symmetrical anodic peak at –0.41 V and another one at +0.03 V on the reverse scan. The reverse scan behavior is typical of a reoxidation of a thin film deposited onto the electrode surface. Such behavior is important for the deposition step in stripping voltammetry. The anodic peak at –0.41 V can be attributed to oxidation of lead and another one at +0.05 V can be attributed to copper oxidation. When the signals, obtained on bare and modified GCE, are compared, they show that the anodic peak for lead was 2.5 times more intense on the modified electrode. The presence of chloride ions additionally improves the voltammetric behavior of lead.[38,39] The shape of the copper signal was more sharp on the modified electrode and it shifted
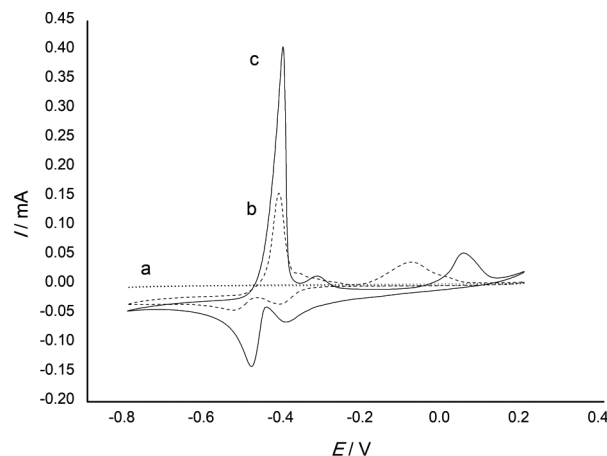

Fig. 1   Cyclic voltammogram of 0.1 mol dm⁻³ HCl/KCl on Nafion/MnCo₂O₄/GCE (a) and with addition of 1 mmol dm⁻³ Pb and Cu on bare (b) and modified GCE (c). Experimental conditions: E_{initial} = 0.2 V, E_{high} = 0.2 V, E_{low} = –0.8 V, scan rate 50 mV s⁻¹.

Table 3   Effect of the sample dilution on lead and copper responses in red wine sample

Sample dilution (v/v)[a]	HCl/ mol dm⁻³	Slope/(μA dm⁻³) μg⁻¹	
		Cu	Pb
1/10	0.05	0.022	0.016
2/10	0.1	0.028	0.047
5/10	0.25	0.015	0.023
9/10	0.45	N/A[b]	N/A[b]

a. Previously acidified.
b. N/A, not applicable, slope values were close to zero.

for 300 mV toward more positive values, probably due to stronger bonds with the electrode surface. The difference between stripping peak potentials on the modified electrode for both metals indicated the possibility of their detection. Smaller peaks at –0.4 V in forward scan and at –0.32 V in reverse scan are also visible on voltammograms, and they can be attributed to lead. Additional peaks can be explained by the heterogeneous nature of the modified electrode surface and the different affinity that lead has for the surface.[38,40,41] They are usually present when lead concentration exceeds 1 μmol/dm³.[40]

In order to achieve the best performance for electrochemical determination, the sample dilution, accumulation potential and time were optimized and applied for the determination of metals in wine samples.

Sample dilution

For trace metal analysis in wine samples, both dry ashing and wet digestion procedures are usually performed. Results obtained by those procedures are in good agreement.[1] The wet digestion involves the use of hydrogen peroxide, or its mixture with strong acids, and may even involve the addition of UV digestion.[42] Since the use of hydrochloric acid proved to be enough for decomposition of organic matter in wine samples, the wine samples were acidified with concentrated hydrochloric acid. After filtration, the different volumes (1, 2, 5 and 9 cm³) of acidified samples were transferred into the electrochemical cell (10 cm³) and after addition of potassium-chloride, stripping

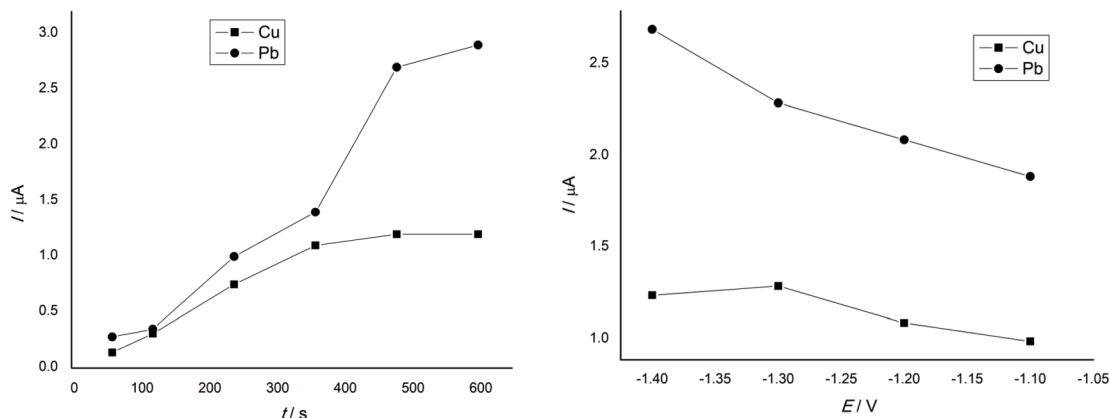Fig. 2   Dependencies of Pb and Cu on accumulation time and potential in wine sample spiked with 25 μg dm^{-3} of Pb(II) and Cu(II).

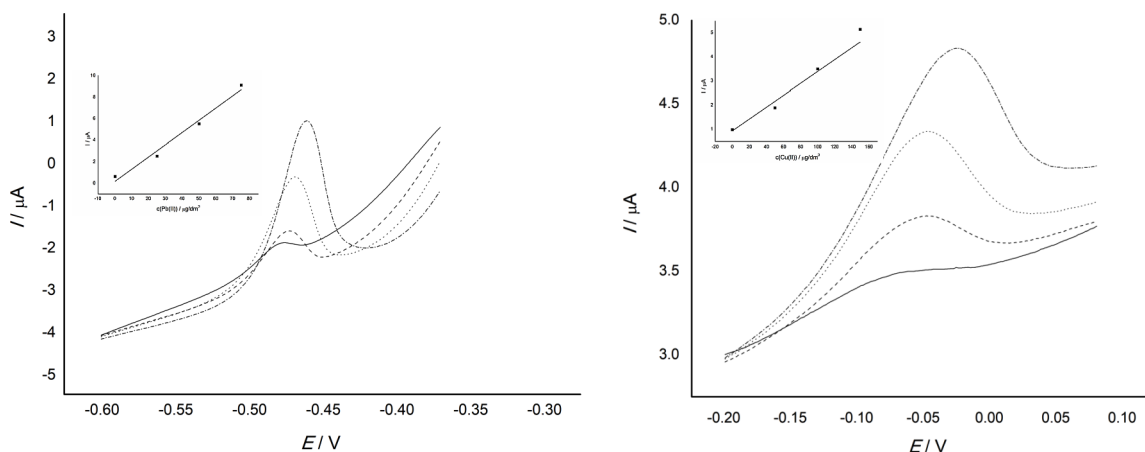Fig. 3   Voltammograms of Pb (left) and Cu (right) on Nafion/MnCo$_2$O$_4$/GCE in a red wine sample. Lead: wine sample +0, 25, 50, 75 μg dm^{-3} Pb(II); Copper: wine sample +0, 50, 100, 150 μg dm^{-3} Cu(II); E_{acc} = −1.4 V, t_{acc} = 480 s, scan rates 50 mV s^{-1}. Insets: obtained calibration curves.

voltammograms were recorded. The results (Table 3) show that the best sensitivity for both analytes was obtained when 2 cm^3 of wine sample was used. When 9 cm^3 of sample was measured, there was no difference in signal intensity when different concentrations of analytes were added, probably due to intense matrix effect. This can be explained by absorption of the organic matter on the electrode surface.[43] Therefore, all experiments were performed when 2 cm^3 of wine sample was diluted with KCl solution so that the final HCl/KCl concentration was 0.1 mol/dm^3.

The accumulation potential and time

The dependence of the anodic stripping current on the accumulation time was examined. The peak current increased with increasing accumulation time, as expected. For deposition times longer than 360 s for copper and 480 s for lead, the stripping signals became almost constant (Fig. 2, left). Since the accumulation time depends on analyte concentration, at lower concentrations it takes a longer time for the current to reach the constant value. On the other hand, at higher metal concentrations, the accumulation is faster and the electrode surface can be saturated in a shorter time. Therefore, the measurement range can be easily controlled by choosing

Table 4   Results of analysis of different wine samples obtained by EC and GFAAS

Wine sample	γ(Cu)/μg dm^{-3}		γ(Pb)/μg dm^{-3}	
	EC	GFAAS	EC	GFAAS
1	79.8 ± 8	85.2 ± 4	17 ± 2	20 ± 2
2	36.2 ± 4	39.3 ± 3	12 ± 1	14 ± 2
3	168 ± 17	174 ± 3	25 ± 3	28 ± 3
4	51.8 ± 5	48.9 ± 5	52 ± 5	48 ± 5
5	42.9 ± 4	45.8 ± 5	15 ± 2	12 ± 2
6	107 ± 11	110 ± 10	2.1 ± 0.6	3.5 ± 1

preconcentration time.   For further experiments, 480 s accumulation time was chosen.

The effect of accumulation potential was investigated in the range from −1.10 to −1.40 V. The concentration of Pb and Cu was 25 μg dm^{-3} and the accumulation time was 480 s. As the accumulation potential became more negative the stripping peak currents increased (Fig. 2, right). When the accumulation potential was more negative than −1.4 V, the stripping peak currents for both lead and copper were unstable due to hydrogen
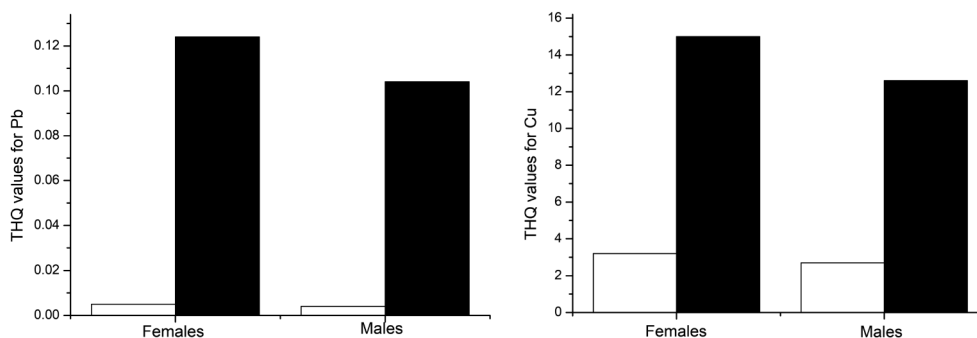
Fig. 4   The THQ values calculated for red and white wine samples based on lead (left) and copper content (right), for minimum and maximum values, for both females (F) and males (M).

evolution at those potentials.   Therefore, considering the satisfactory sensitivity, the potential of –1.4 V was chosen for the following investigations.

Interferences

According to our previous investigations, the $MnCo_2O_4$ material was found to have a high surface area to volume ratio and an open porous structure with more active sites for heavy metal accumulation.   It exhibited high sensitivity, selectivity and a wide concentration linear range for the determination of cadmium and lead.[34]   Copper ions interfered in the quantification of those analytes and the signal for lead decreased by about 40%, such behavior was explained by the presence of the sulfate ions, and its effect on copper ions conductivity.   For the wine samples, sulfuric acid was avoided, and the oxidation current for copper was significantly lower than for the lead even though it is a metal found in abundance in the wine samples (Fig. 1).   However, the difference in oxidation potential (around 450 mV) enabled selective determination of these analytes.

The effect of various ions on lead and copper determination was investigated.   The presence of Mn, Hg, Cr, Ni, Fe, K, Mg, Ca, Ba in excess did not affect the signals for Pb and Cu.   The electrode was sensitive to the presence of Cd and Zn but their presence did not interfere in the stripping current for Pb and Cu.   Introduction of Nafion, a perfluorosulfonated ionomer that is water insoluble and permeable with size/exclusion properties, prevented the fouling of the electrode surface and increased sensitivity of the sensor towards lead and copper in a complex matrix sample such as wine samples.   The use of Nafion enhanced the stability of the sensor compared to our previous work.[34]   The sensor was used for 30 measurements before the recovery decreased by more than 95%.

Analytical parameters

Under optimized conditions, the linearity, limit of detection (LOD) and limit of quantification (LOQ) were evaluated through external calibration.   The sensor gave a linear response for concentrations 0.01 – 8 and 0.01 – 5 mg dm^{-3} for Pb and Cu, respectively.   LOD was calculated as $3S/b$, where S is the standard deviation of the intercept and b is the slope.   LOQ was calculated as $10S/b$.   Obtained LOD values were 1.67 and 7.14 μg/dm^3 and LOQ values were 5.5 and 23.6 μg dm^{-3} for Pb and Cu, respectively.   The reproducibility of the sensor was evaluated by 10 repetitive measurements of Pb and Cu.   The relative standard deviations were 1.5 and 1.8% 25 μg dm^{-3} for Pb and Cu, respectively.

Determination of copper and lead in wine samples

Copper and lead in wine samples were determined by standard addition method.   Under optimized conditions (sample dilution, accumulation potential and time), analytes were quantified by the addition of 25, 50, and 75 μg dm^{-3} of lead and 50, 100, and 150 μg dm^{-3} of copper (Fig. 3).   The corresponding equations were $I(\mu A) = 0.111c(\mu g\ dm^{-3}) + 0.047$ ($r = 0.985$) for lead and $I(\mu A) = 0.028c(\mu g\ dm^{-3}) + 0.600$ ($r = 0.982$) for copper in a red wine sample (sample 1, Table 1).   Results obtained for electrochemical determination of these metals are presented in Table 4.   According to the *Office International de la Vigne et du Vin* (OIV),[44] the allowed concentrations of copper are 1 mg dm^{-3} and 150 μg dm^{-3} for lead.   As it can be seen, all concentrations were lower than those allowed by OIV.   Results obtained by electrochemical method were compared to results obtained by GFAAS (Table 4), which allows quantification of the metal contents.   There was significant agreement of the results obtained by the two methods, and it was confirmed by Student t-test.   For the 95% confidence level ($n = 5$), t-test values were lower than the theoretical value (2.776), confirming that the difference between the results is insignificant.

Target hazard quotient estimation

Target hazard quotients were introduced by the Environmental Protection Agency (EPA) for estimation of potential health risks caused by long term exposure to pollutants.   It is a ratio between the measured concentration and the oral reference dose, taking into account the length and frequency of exposure, ingested amount and body weight.   Copper and lead are representatives of two different groups of metals.   Copper is a key nutrient that needs to be introduced into an organism by dietary sources, while lead presents a toxic heavy metal, the ingestion of which at high levels can cause serious health problems.   The measured copper and lead concentrations by electrochemical method were used to calculate THQ using Eq. (1).   The THQ values were calculated for both males and females, based on the average life expectancy of 81.9 and 84.7, respectively, from 18 years of age and on, and mean weight of 83.11 and 69.81 kg respectively, in the case of one large glass of wine (250 cm^3) consumed daily; using oral reference dose for lead of 1.5 and for copper of 0.04 mg per kg per day.[36,37]   For the oral reference doses, the highest average daily intake levels with no risk to human health were used.   The obtained THQ values for all wine samples, for both male and female consumers, were below 1 for lead which means that the negative effects are neglible (Fig. 4).   The THQ values for copper were in the range 2.7 – 12.63 for male and 3.2 – 15.04 for female consumers.   Since copper is a bioelement that is important for normal functioning of some metalloenzymes,

the increased amount of copper does not present health risks. The safe amount of dietary copper intake for adults is 40 µg per kg per day.[45]

Conclusions

MnCo$_2$O$_4$ nanoparticles were used as non-toxic modifiers for voltammetric determination of copper and lead in different wine samples. The simple sample preparation consisted of acidification of samples by hydrochloric acid and subsequent filtration. One modified electrode was used for 30 measurements. Obtained results were compared to the results obtained by GFAAS and they showed good agreement.

Acknowledgements

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