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Extraction and quantification of pesticides and metals in palm wines by HS-SPME/GC-MS and ICP-AES/MS

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ABSTRACT

In this study, a HS-SPME/GC-MS and ICP-AES/MS methods are presented to extract and quantify pesticides and metals in palm wines. Various parameters affecting the extraction were investigated: SPME fiber, equilibrium and extraction time, extraction temperature, salinity, and stirring, through an experimental design with 45 trials. The developed method allowed to identify 35 pesticides and quantify 29 of them, from different families of pesticides in 32 palm wine samples. Method performance was evaluated in terms of linearity, repeatability, LOD, LOQ, and accuracy. Among the 32 samples analyzed in 3 replicates, 7 pesticides were detected in 10 samples. Dichlorvos was the only pesticide detected at levels above the European maximal limits. Additionally, 10 of the 19 metals explored by ICP-AES and ICP-MS were found in all

samples. Six metals were detected in different samples at levels above the European or OIV maximal limits for drinking water or wine.

Keywords: palm wine, pesticides, metals, headspace solid-phase microextraction, gas chromatography, mass spectrometry, induced coupled plasma mass spectrometry

1. Introduction

Palms are believed to be among the oldest flowing plant in the world (Redhead, 1989). The oil palm (*Elaeis guineensis Jacq*.) is one of the major cultivated crops among the economically important palm species. Their growth is so vigorous that they are considered as a "weed" in neglected or abandoned farms. Different parts of the palm tree can be used for various purposes, but one important commercial activity associated with the tree is production of wine from the sap by the local populations (Yaméogo et al. 2008). Yet the oil palm in West Africa is highly valued for palm wine production, and could allow farmers to supplement and diversify their incomes. As an example, in western Ivory Coast, the resumption of wild oil palm in old cocoa farms played an important role in the 1990s, when farmers faced collapsing cocoa prices and inheritance conflicts, which resulted in the abandonment of many cocoa plantations where the density of oil palms trees grew rapidly. Thus, the felling of palm trees made it possible to produce palm wine for sale and for own consumption, thus generating income, reducing risks and creating jobs and new intergenerational and institutional arrangements (Ruf, 2014).

Palm wine is the collective name for a group of alcoholic beverages produced by the natural fermentation of the sap obtained from various tropical plants of the Palmae family (Okafor, 1978), such as Elaeis guineensis, Raphia hookeri, Phoenix dactylifera, B. aethiopum and Cocos nucifera (Mollet et al. 2000; Sambou et al. 2002; Stringini et al. 2009; Ziadi et al. 2011). It is mainly consumed by more than 10 million people in West Africa (Battcock et al., 1998) but it

is also available in Asia, India and Mexico (Chandrasekhar et al., 2012). A study by Fatoye and Morakinyo (2002) on alcoholic drinks (beer, locally fermented wine and locally distilled gins) in West Africa showed it as the most commonly used alcoholic beverages. It serves a variety of purposes, notably in traditional namings and marriage ceremonies, medicine (cure of low sperm count and poor sight), traditional incantation and also acts as catalyst for extraction of juice from herbs and roots for medical application.

Generally, the palm sap for palm wine production is obtained through a process known as tapping, operated in open-air, and involving a series of operations on live standing or felled or cut down tree, such as perforation of the trunk, insertion of a tube in the hole and collection of the sap in a container which can be a gourd, clay pot, plastic container, glass bottle or calabash as previously reported (Ouoba et al., 2012). The tapping process between 2 and 8 weeks and palm wine is collected twice a day (early in the morning and in the evening) and either immediately consumed on fields or stored for later sale.

Despite the enormous economic, medicinal and socio-cultural importance attached to the production of palm wine in rural African society, the consumption of this drink is becoming increasingly problematic because of two major facts. Indeed, it becomes fearful on the one hand, and this is a recurring observation, to frequent the palm wine from cabarets. This fear is generated by the fact that crooked sellers tend to sell an adulterated version of the drink, resulting from the adulteration of the original palm wine by using water (generally of low quality with a distinct possibility of contamination with undesirable elements such as metals) and artificial sweetness, which sometimes result in diarrhea, abdominal pains, and other stomach problems (Ukhun et al. 2005). In other hand, as palm trees mostly grow concomitantly in cocoa farms in rural areas, the second problem and hence the quieter comes from the potential contamination of this drink during tapping process by pesticides or their residues used in the agrochemical treatments of cocoa fields in which the sap extraction process takes place. Indeed,

in an attempt to reduce the incidence of insect pests and diseases on cocoa farms, a large number of pesticides are usually applied on farms. These pesticides are hazardous in very low concentrations and cause immense damage to the ecosystem. In most developing countries like Ivory Coast, consequences are often severe because approved pesticides are not used and recommended frequencies of pesticides application by government agencies for crops are not followed. Farmers however misuse, overuse and apply pesticides indiscriminately with disregard to safety measures and regulations on chemical use as reported by Konradsen (2007) and Sam et al. (2008). In consequence, the drink produced can be contaminated at multiple steps in the tapping process by plant material treated with pesticides, particularly leaves used to cover containers containing the drink in the palm wine processing environment, or insects when flying into bowls. According to the National Pesticide Information Center (2011), an increase in the use of agrochemicals has been observed over the past fifty years making humans more exposed to heavy metals, pesticides and insecticides. Heavy metals and pesticides have carcinogenic, mutagenic and teratogenic potential and exposure can cause irreversible damage to humans, including death, and are therefore considered a serious public health problem particularly in sub-Saharan countries. Although many studies have revealed that pesticides and heavy metals poses threats to the environment, and farmers themselves, their potential presence in palm wine and the risks associated have to be determined.

Several methods are available for extraction and quantification of pesticides and metals from complex matrices. For pesticides, liquid extraction with solvents, such as dichloromethane, acetone (Gambacorta et al., 2005), and ethyl acetate (Munawar and Waqas Hameed, 2013) has been used. Pesticide residues have also been extracted from apple juice using a solid phase extraction (SPE) method (Han et al. 2014; Velkoska-Markovska and Petanovska-Ilievska, 2013), from berry fruits using an Envi-Carb cartridge (Yang et al, 2011) and using an HS-SPME method, a fast, automatable, and inexpensive method, including in mangoes from Brazil (Filho,

Dos Santos, and De Paula Pereira 2010), in water samples from Argentina (Bonansea, Amé, and Wunderlin 2013) and in wines from Italy (Vitali et al. 1998). In general, the analysis of pesticides is done using gas (Han et al., 2014 and Yang et al., 2011) or liquid (Velkoska-Markovska and Petanovska-Ilievska, 2013) chromatography, depending on the polarity, volatility and decomposition risk of the compounds. For the detector, the electron capture detector is commonly used to quantify organochlorines, while the nitrogen-phosphorus detector is used for organophosphates. Mass spectrometry offers the advantage of being able to identify and quantify a wide range of molecules, without being limited to a single class of pesticides (Bonansea, Amé, and Wunderlin 2013). Metals are commonly analyzed by ICP-AES/MS in pharmaceutical compounds (Lewen et al., 2004), textile materials (Rezić and Steffan, 2007), or wines and alcoholic beverages (Płotka-Wasylka et al., 2018), due to sensitivity, low limit of detection and speed of analysis. Prior to analysis, samples are mineralized to remove organic matter and ensure quantitative dissolution of metals in the case of solid matrices. Most of the time, acids or acid mixtures are used for this step (Lewen et al., 2004): nitric acid, hydrochloric acid, sulfuric acid, or mixtures, with aqua regia being the most famous. Due to the low detection levels required by regulatory agencies, efficient sample preparation and trace-level detection are important aspects in an analytical method.

This research was therefore conducted to determine the concentration of heavy metals and pesticides using optimized methods and then raise awareness of the possible health risk while consuming this beverage.

2. Materials and methods

2.1 Chemicals

Ultrapure water (resistivity 18.2 MW•cm), obtained from a Milli-Q system (Millipore, Bedford, MA, USA), sodium sulfate (GPR Rectapur, VWR Chemicals, Belgium), ethanol (99%, Fisher

Scientific, UK), (+) limonene (97%, Accros Organics, USA) decane (99%, Sigma-Aldrich, USA), L-ascorbic acid (99%, VWR Chemicals, Belgium), calcium chloride (98%, VWR Chemicals, Belgium), potassium chloride (99%, Carlo Erba, Italia), magnesium nitrate (98%, Sigma-Aldrich, USA), and sodium chloride (99.5%, Acros Organics, USA), were used for the preparation of the simulative palm wine. For the mineralizations, nitric acid (68%, trace analysis grade, Fisher Scientific, UK) and hydrogen peroxide (30%, VWR Chemicals, Belgium) were employed. Acetone (pesticides residue grade, Fisher Scientific, UK) and methanol (HPLC grade, Fisher Scientific, UK) were used for the preparation of the stock solutions of pesticides.

The pesticides standard consisted in six stock solutions. Two solutions were purchased from Restek (USA): an OrganoPhosphorus Pesticides (OPPs) solution in acetone containing acephate (200 µg mL^{-1}), azinphos methyl (400 µg mL^{-1}), chlorpyrifos (100 µg mL^{-1}), demeton-S-methyl (200 µg mL^{-1}), dichlorvos (500 µg mL^{-1}), dimethoate (200 µg mL^{-1}), ethion (200 µg mL^{-1}), malathion (200 µg mL^{-1}), methamidophos (500 µg mL^{-1}), methidathion (200 µg mL^{-1}), omethoate (1,000 µg mL^{-1}), pirimiphos methyl (100 µg mL^{-1}), profenofos (200 µg mL^{-1}), prothiofos (200 µg mL^{-1}), pyrazophos (500 µg mL^{-1}), and tolclofos-methyl (100 µg mL^{-1}), and an organohalide pesticides solution in methanol containing aldrin, alachlor, atrazine, γ-BHC (lindane), cis-chlordane, trans-chlordane, dieldrin, endrin, heptachlor, heptachlor epoxide (isomer B), hexachlorobenzene, hexachlorocyclopentadiene, methoxychlor, cis-nonachlor, trans-nonachlor, and simazine, at 200 µg mL^{-1} each. Two solutions were purchased from Fisher Scientific (France): an OrganoChloride Pesticides (OCPs) solution in acetone containing aldrin, α, β and δ-BHC, dieldrin, α and β-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, lindane, heptachlor, heptachlor epoxide (isomer B), methoxychlor, p,p'-DDD, p,p'-DDE, and p,p'-DDT at 200 µg mL^{-1} each, and a terbutylazine solution in acetone at 100 µg mL^{-1}. A methyl parathion solution in acetone at 1000 µg mL^{-1}, and a diazinon solution in methanol at 100 µg mL^{-1} were purchased from Merck (Germany).

The stock solution containing all pesticides was prepared in pure acetone and before each serie of analyses. The pesticides standard solutions at different levels were prepared by spiking with the stock solution into 3 mL of the simulative palm wine contained in a 20 mL sealed glass vial.

Calibration curves were prepared from dilutions of the stock solution. The concentration of pesticides ranged from 0.25 µg L^{-1} for pirimidiphos methyl and tolclofos-metyl to 1000 µg L^{-1} for simazine.

A metal solution (VWR Chemicals, Leuven, Belgium) containing aluminum, silver, arsenic, boron, barium, calcium, cadmium, cerium, cobalt, chromium, copper, dysprosium, erbium, europium, iron, gadolinium, holmium, potassium, lanthanum, lithium, lutetium, magnesium, manganese, sodium, neodymium, nickel, phosphorus, lead, rubidium, selenium, samarium, strontium, thallium, thulium, vanadium, and zinc, at 10 mg L^{-1} each, was used. Three mono-element solutions containing bismuth at 10 mg L^{-1} (Spex CertiPrep, USA), molybdenum (Spex CertiPrep, USA) and tin at 1000 mg L^{-1} (Fisher Scientific, France) were used for preparing the stock solutions. Calibration curves were prepared from dilutions of the stock solution. The concentration of metals ranged from 0.05 µg L^{-1} to 100 µg L^{-1} for all metals except for rubidium which ranged from 0.05 to 2 mg L^{-1} and for phosphorus which ranged from 0.5 to 20 mg L^{-1}.

2.2 Samples

This study was carried out on different palm wines produced in four cities in Ivory Coast (Abidjan, Aboisso, Hiré and Toumodi). Four samples of each city were collected from local producers (P) and four from resellers (R), who could eventually modify the composition of the palm wines. Thirty two palm wines were analyzed (3 replicates) for determination of pesticides and metals. Samples were stored in a freezer at -18°C. Before analysis, samples were kept at 4°C during two hours in a fridge and thirty minutes at room temperature. The palm wines presented particles naturally present. To estimate the real concentrations to which the population is exposed, it was decided to let the samples as naturally present and consumed.

Consequently, no filtration nor centrifugation was done, and the samples were mixed before analysis in triplicate.

2.3 Instrumentation

2.3.1 GC-MS

Analyses of palm wine were performed using a GC-MS QP-2020 NX (Shimadzu, Germany) equipped with an auto-sampler AOC-6000 (automatic injection). Different GC conditions for analyzing pesticides were tested; to find a good compromise between the analysis time and the resolution. As final GC conditions, a ZB5MS+ (5% polysilarylene and 95% dimethylpolysiloxane, 30 m x 0.25 mm x 0.25 µm, Phenomenex) column was used to separate pesticides; helium was used as carrier gas (1 mL/min); injection was splitless and at 260°C. The oven temperature was programmed as follows: initially maintained at 40°C (held for 5 min), then increased to 180°C (held for 2 min) at a rate of 10°C/min, a second increase was used to 280°C (held for 2 min) at a rate of 5°C/min. The optimal analysis time was 43 minutes.

The MS transfer line was kept at 250°C. The mass spectrometer, equipped with a quadrupole mass filter, was in the electron impact ionization mode (70 eV) with an ion source temperature of 200°C. Chromatograms were acquired in Single Ion Monitoring (SIM) scaning mode. The m/z associated with pesticides are specified in Table S1. All compounds could be separated excepted cis and trans chlordane. These isomers were identified on the same peak. Moreover, MS was not able to identify with certainty the three BHC (hexachlorocyclohexane), the three isomers were identified as BHC on chromatograms.

2.3.2 ICP-AES and ICP-MS

Extraction and mineralization of samples were performed with a Milestone ETHOS 1 microwave digestion system equipped with a temperature sensor. TFM reactors were used with a maximum pressure of 100 bar. ICP-AES measurements were performed on an iCAP 6300

series instrument (Thermo Fisher Scientific) using the axial view. The quantification of phosphorus and rubidium was performed at 178 nm and 780 nm, respectively.

Detection of lithium, boron, chromium, iron, manganese, cobalt, nickel, copper, zinc, strontium, molybdenum, silver, cadmium, tin, barium, lead, and bismuth was performed on an iCAP RQ ICP-MS instrument (Thermo Fisher Scientific) fitted with a collision cell. Two different measurement modes were used: standard mode (STD) and kinetic energy discrimination mode (KED). In the KED mode, Helium gas was injected in the collision cell and an energy discrimination barrier was applied in order to remove unwanted polyatomic interferences. Data processing was performed using ThermoFisher Scientific Qtegra software.

As example, optimized conditions for the plasma and nebulizer for ICP-AES and ICP-MS are given in Table S2.

2.4 Method optimization

2.4.1 The simulative palm wine

Because of the low volume of palm wine samples, a surrogate matrix (simulative palm wine) was developed to determine HS-SPME/GC-MS optimal conditions before application on real samples.

For this purpose, a palm wine sample was analyzed by GC-MS to determine the main constituents. It was found that palm wine contained around 88 % (m/m) of water, 2 % (m/m) of ethanol, and 10 % (m/m) of sucrose. Based on a previous study on palm wines (Simon Amoikon et al., 2020), the aromatic profile was recreated using 4 mg L^{-1} of limonene and 10 mg L^{-1} of decane, main compounds found in real palm wines. Calcium (5 mg L^{-1}), potassium (280 mg L^{-1}), magnesium (7 mg L^{-1}) and sodium (4 mg L^{-1}) concentrations were determined in the palm wine sample by ICP-AES. According to Cunningham and Wehmeyer (1988), vitamin

C (60 mg L^{-1}) is generally added. Finally, the simulative palm wine was doped to achieve the concentrations generally found in such samples.

2.4.2 Optimization of the HS-SPME procedure

Experimental parameters were evaluated to determine the optimal conditions for the analysis of pesticides in palm wines. Three fiber types were tested: 100 µm polydimethylsiloxane (PDMS), 85 µm polyacrylate (PA), and 50/30 µm DVB/Carbon WR/PDMS (Restek USA). Fibers were conditioned at 230°C during 30 min before each analysis, according to the manufacturer's recommendations. Three milliliters of the simulative palm wine were placed in a 20 mL sealed headspace glass vial (3 replicates). After extraction, the fiber was automatically retracted and transferred to the GC injector at 260 °C for a desorption time of 3 min.

In order to optimize the extraction efficiency, an experimental design (Table S3) with 45 trials was implemented (Ellistat software, Chavanod, France) on a 100 µm PDMS fiber. Some parameters were tested, according to the literature for pesticides extraction by HS-SPME. Extraction temperature between 30 and 60°C (Cincotta et al., 2015), equilibrium time between 5 and 30 min (Bernardi et al. 2015, Pellati et al. 2013), and extraction time between 20 and 60 min (Pellati et al., 2013) were investigated. Moreover, stirring was studied between 250 and 500 rpm (Filho et al., 2010, Bernardi et al. 2015), and salinity (sodium sulfate) between 5 and 15 % (m/m) (Vitali et al., 1998, Zhu et al., 2009) of the sample. According to Zhu et al (2009), who worked on the determination of OPPs in textiles using SPME coupled with GC/MS, OPPs were more extracted with sodium sulfate than with sodium chloride.

Data processing was performed using the GC-Solution software.

2.5 Method validation

2.5.1 Analysis of palm wine by HS/SPME-GC/MS

For the study of pesticides in complex matrix, an HS-SPME extraction technique was used. As final conditions after optimization, a 20 mL vial was filled with 3 mL of each palm wine samples (3 replicates) and 7.5 % (m/m) of sodium sulfate. Extraction was done in the headspace vial kept at 52.5°C. A DVB/C-WR/PDMS fiber was used for all extractions because it allowed the determination of many pesticides with good repeatability (see results and discussions - fiber coating). The palm wine samples were equilibrated for 11.25 min and extracted for 50 min under continuous stirring (437.5 rpm). The fiber was automatically transferred to the GC injector at 260 °C for desorption time of 3 min. The method performance was evaluated in terms of linearity, limit of detection, limit of quantification, accuracy, and precision (repeatability).

The concentration of three stock solutions ranged from 0.5-2.5 μg L^{-1} (for Tolclofos-methyl and Dichlorvos, respectively) to 5-25 μg L^{-1} (for Tolclofos-methyl and Dichlorvos, respectively). These three stock solutions were each injected three times in order to study the repeatability (represented by a relative standard deviation (RSD)). To study the linearity, calibration curves with 3-5 points were established. LOD and LOQ were estimated as concentrations of pesticides which allowed a signal-to- noise ratio (S/N) of 3 and 10, respectively. Additionally, samples were spiked with stock solutions (to obtain three samples with concentrations from 0.5-2.5 μg L^{-1} (for Tolclofos-methyl and Dichlorvos, respectively) to 5-25 μg L^{-1} (for Tolclofos-methyl and Dichlorvos, respectively) three times and relative recoveries were determined.

2.5.2 Analysis of palm wine by ICP/AES and ICP/MS

In accordance to the French standard « » for the determination of metals in drinking water, ICP-MS is the reference technique and is used after mineralization. No standard exists for palm wine, and it consists of 88% water, so the same methodology was followed and can be assimilated to drinking water.

A volume of 2 mL of palm wine was digested with 2 mL of nitric acid and 1 mL of hydrogen peroxide in a microwave system: from room temperature, 30 ºC, to 180 ºC, 20 minutes at 180

ºC. After the mineralization, the digest was diluted up to 50 mL with ultrapure water. A blank was analyzed in the same conditions.

Samples were analyzed with ICP-AES for the determination of phosphorus and rubidium, and with ICP-MS for the determination of the other metals. To study the linearity, calibration curves with 5 points were established.

LOD and LOQ were obtained for the palm wine samples using equations 1 and 2, where BEC is the background equivalent concentration (µg L^{-1}), it represents the blank intensity divided by the angular coefficient of the analytical curve and RSD_{blank} is the relative standard deviation of the blank (n=10).

$$LOD = \frac{3\ x\ RSD_{blank}\ x\ BEC}{100} \quad \text{(Equation 1)}$$

$$LOQ = \frac{10\ x\ RSD_{blank}\ x\ BEC}{100} \quad \text{(Equation 2)}$$

3. Results and discussion

3.1 Determination of pesticides in palm wines

3.1.1 Determination of SPME conditions

Different parameters were tested in order to develop a HS/SPME-GC/MS method with the optimized extraction efficiency. Fiber coating, extraction temperature, equilibrium time, extraction time, stirring, and salinity were studied.

3.1.1.1 Extraction temperature, equilibrium and extraction time, stirring and salinity

Five parameters have been explored in this study on a 100 µm PDMS fiber: extraction temperature, equilibrium and extraction time, stirring and salinity. Among the 45 trials of the experimental design, one offered the highest peak area for 7/12 extracted pesticides of the OPPs solution (azinphos methyl, chlorpyrifos, ethion, methidathion, pirimiphos methyl, profenofos and tolclofos methyl). This method had a long extraction time and according to the exploitation

of the experimental design, the extraction time was the parameter that influences the most the extraction efficiency.

Finally, the extraction temperature was set at 52.5°C. Increasing the temperature allows reducing the extraction time, which increases the concentration of semi-volatiles in the vial headspace (Bianchin et al., 2014). Pesticides were mostly obtained with high peak areas for an extraction temperature of 52.5°C. Lowers peak areas were obtained with a temperature of 37.5°C (comparison of trials 4 and 8 in Table S3, parameters were set at the optimized values, except for extraction temperature), especially for chlorpyrifos (peak areas of 889083 and 3829688 for temperatures of 37.5°C and 52.5°C, respectively), ethion (peak areas of 18863 and 2459896 for temperatures of 37.5°C and 52.5°C, respectively), and tolclofos methyl (peak areas of 6788178 and 21189553 for temperatures of 37.5°C and 52.5°C, respectively.

Equilibrium time was set at 11.25 min. Equilibrium time depends on the chemical nature and physico-chemical parameters of pesticides. The optimum equilibration time was selected as the time ensuring the highest peak area for the majority of pesticides (all other parameters being constant), with a reasonable time. Finally, 11.25 min was selected for equilibration time.

The highest extraction time tested with the experimental design was 60 min. A higher extraction efficiency was observed for a higher exposure time between the SPME fiber and the sample headspace (Ho and Hsieh, 2001), but a longer exposure could also damage the fiber and/or the pesticides. The extraction time of 50 min was a compromise between extraction efficiency and fiber lifetime and/or pesticides stability. This extraction time was compared with a lower time of 30 min (trials 6 and 8). All other parameters were constant at the optimized values. Pesticides were mostly obtained with high peak areas with an extraction time of 50 minutes. Ethion (peak areas of 744276 and 2459886 for times of 30 min and 50 min, respectively), and prothiofos (peak areas of 1725649 and 3690958 for times of 30 min and 50 min, respectively) were more extracted with the higher extraction time. However, malathion was more extracted with the

lower extraction time (peak areas of 502458 and 198595 for times of 30 min and 50 min, respectively).

Stirring and salinity of the sample allows the diffusion layer to reach the equilibrium faster (Ho and Hsieh, 2001). Stirring of 437.5 rpm and 7.5% (m/m) of Na_2SO_4 allowed to reduce the analysis time, by promotion of the pesticides from the liquid phase to the gas phase.

Finally, SPME optimized parameters for this study were: an extraction temperature of 52.5°C, an equilibrium time of 11.25 min, an extraction time of 50 min, stirring of 437.5 rpm, and salinity of 7.5% of Na_2SO_4.

3.1.1.2 Fiber coating

Three SPME fiber coatings were used to extract the pesticides in the simulative palm wine solution: a 100 µm polydimethylsiloxane (PDMS), a 85 µm polyacrylate (PA), and a 50/30 µm DVB/Carbon WR/PDMS. Compounds were spiked between 2.5 to 12.5 µg L^{-1} triplicate. SPME optimized parameters (see 3.1.1.1 Extraction temperature, equilibrium and extraction time, stirring and salinity) were used.

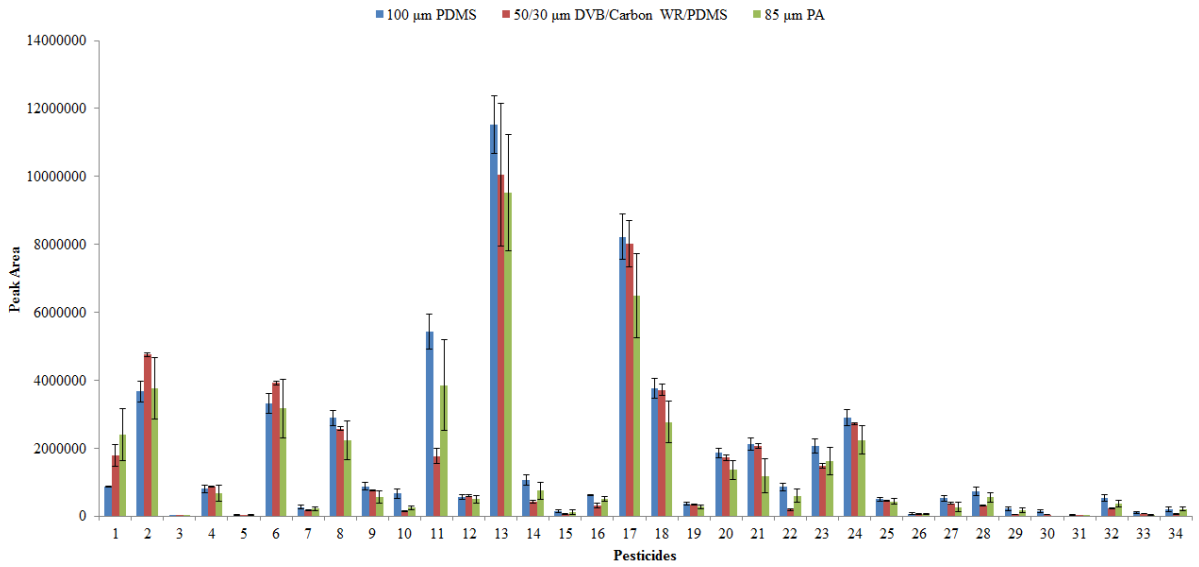


Fig.1. Comparison of three SPME fiber coatings for the extraction of 35 pesticides. Peaks: (1) dichlorvos, (2) BHC, (3) simazine, (4) BHC, (5) atrazine, (6) lindane, (7) terbuthylazine, (8) diazinon, (9) BHC, (10) parathion methyl, (11) tolclofos methyl, (12), alachlor, (13) heptachlor, (14) pirimiphos methyl, (15) malathion, (16) chlorpyrifos, (17) aldrin, (18) heptachlor epoxide,

(19) α-endosulfan, (20) chlordane, (21) trans-nonachlor, (22) prothiofos, (23) p,p'-DDE, (24) dieldrin, (25) endrin, (26) β-endosulfan, (27) cis-nonachlor, (28) p,p'-DDD, (29) ethion, (30) endrin aldehyde, (31)endosulfan sulfate, (32) p,p'-DDT, (33) endrin ketone, (34) methoxychlor. Hexachlorobenzene was not represented because its area was too important.

The three SPME fibers allowed the extraction of all pesticides as it can be observed from Table S4, except for the endrin aldehyde, which was not extracted by the PA fiber. The detector was saturated and no longer able to give an area for hexachlorobenzene using the DVB/Carbon WR/PDMS fiber. Some pesticides had low peak areas no matter the fiber, such as simazine, atrazine, malathion, β-endosulfan, endrin aldehyde, endosulfan sulfate or endrin ketone. Twenty-eight pesticides were extracted with higher area with the PDMS fiber, 5 with the DVB/Carbon WR/PDMS fiber and 2 with the PA fiber. A lot of pesticides were extracted with an important area with PDMS and DVB/Carbon WR/PDMS fibers, such as aldrin (peak area of 8228026 for the PDMS fiber and 8021739 for the DVB/Carbon WR/PDMS fiber), diazinon (peak area of 2886678 for the PDMS fiber and 2577749 for the DVB/Carbon WR/PDMS fiber), or heptachlor (peak area of 11522371 for the PDMS fiber and 10058902 for the DVB/Carbon WR/PDMS fiber).

However, as shown in Table S4, the DVB/Carbon WR/PDMS fiber exhibited the lowest RSDs for 25 pesticides (RSDs between 0.7 and 18%) and offered 22 RSDs under 10%. Only 14 and 1 RSDs were under 10% for the PDMS and PA fibers, respectively. The best repeatability was achieved with the DVB/Carbon WR/PDMS fiber. Therefore, this fiber was selected for the analysis of palm wines.

3.1.2 Analysis of palm wine samples

3.1.2.1 Method validation

3.1.2.1.1 Quadratic or linear behavior of calibration curves

Initially, a linear calibration model was developed for all pesticides. This type of calibration is the most used to obtain an analytical result from the measurement of the signal. According to Balsini and Parastar (2019), pesticides may have a quadratic behavior. In this study, 12 pesticides (aldrin, chlordane, α-endosulfan, endrin heptachlor, heptachlor epoxide, parathion methyl, pirimidiphos methyl, prothiofos, p,p-DDD, and simazine), followed a quadratic calibration curve and 23 of them had a linear behavior. The analytical results were listed in Table 1 (linear (L) or quadratic (Q) behavior, LODs, and LOQs).

Table 1

Quadratic or linear behavior, LODs, and LOQs of pesticides in this study and results from the literature

No.	Pesticides	Behavior [a]	Range (μg L^{-1})	R^2	LOQs (μg L^{-1})	LODs (μg L^{-1})	LODs from the literature (μg L^{-1})	LOQs from the literature (μg L^{-1})	Fiber used from literature
1	Dichlorvos	L	1.25-250	0.9999	1.25	0.11	0.05		85 μm PA [27]
							3.80	11.4	65 μm PDMS/DVB [25
2	BHC	L	1-100	0.9998	0.31	0.09			
3	Hexachlorobenzène	L	0.5-5	0.9971	0.10	0.03			
4	Simazine	Q	100-1000	1	92.1	27.6	0.10		85 μm PA [27]
5	BHC	L	0.5-100	0.9999	0.20	0.10			
6	Atrazine	L	10-1000	0.9993	10.0	3.00			
7	Lindane	L	2-200	0.9999	0.11	0.03			
8	Terbuthylazine	L	1-100	0.9999	1.00	0.30			
9	Diazinon	L	5-100	0.9998	0.58	0.17	3.00		85 μm PA [33]
							0.01		85 μm PA [27]
10	BHC	L	0.5-100	0.9999	0.75	0.22			
11	Parathion methyl	Q	0.5-10	0.9991	0.02	0.01	50.0		85 μm PA [33]
12	Tolclofos-methyl	L	0.25-5	0.9993	0.13	0.04	0.01		85 μm PA [27]
13	Alachlor	L	1-100	0.9999	0.53	0.16			
14	Heptachlor	Q	1-20	0.9994	0.01	0.003			

15	Pirimidiphos methyl	Q	0.25-50	0.9999	0.25	0.08			
16	Malathion	L	5-100	0.9998	1.20	0.36	45.0		85 µm PA [33]
							10.0		85 µm PA [27]
17	Chlorpyrifos	L	0.5-50	0.9997	0.03	0.01	80.0		85 µm PA [27]
							4.50	13.7	65 µm PDMS/DVB [25
18	Aldrin	Q	1-20	0.9991	0.11	0.03			
19	Heptachlor epoxide	Q	1-20	0.9999	0.08	0.02			
20	α-Endosulfan	Q	0.5-100	0.9999	0.17	0.05			
21	Chlordane	Q	1-20	0.9997	0.16	0.05			
22	trans-Nonachhlor	L	1-100	0.9999	0.01	0.002			
23	Prothiofos	Q	0.5-10	0.9999	0.22	0.07			
24	p.p'-DDE	L	0.5-10	0.9963	0.01	0.003			
25	Dieldrine	L	1-20	0.9996	0.09	0.03			
26	Endrin	Q	1-20	0.9999	1,00	0.03			
27	β-Endosulfan	L	0.5-100	0.9999	0.50	0.15			
28	cis-Nonachlor	L	1-100	0.9999	0.06	0.02			
29	p.p'-DDD	Q	0.5-100	0.9998	0.32	0.10			
30	Ethion	Q	1-100	0.9999	0.62	0.18	2.20	6.50	65 µm PDMS/DVB [25
31	Endrin aldehyde	L	0.5-100	0.9999	0.50	0.15			
32	Endosulfan sulfate	L	1-100	0.9999	1,00	0.30			
33	p.p'-DDT	L	0.5-100	0.9999	0.07	0.02			
34	Endrin ketone	L	0.5-100	0.9999	0.50	0.15			
35	Methoxychlor	L	1-20	0.9997	1.00	0.30			

[a] Q = quadratic calibration, L = linear calibration

All calibration curves had correlation coefficients between 0.9963 and 1, therefore, the quantification of pesticides in palm wines was acceptable.

3.1.2.1.2 LODs and LOQs

The obtained LODs ranged between 0.002 and 27.6 μg L^{-1}, for trans-nonachlor and simazine, respectively, and LOQs ranges between 0.01 and 92.05 for p,p'-DDE and simazine, respectively. For such compounds, some comparisons can be done with literature. For example, for the Dichlorvos, LOD with the optimized method was 0.11 μg L^{-1}, Sakamoto and Tsutsumi found a LOD of 0.05 μg L^{-1} in water sample with a 85 μm PA fiber, and Rodrigues et al found a LOD of 3.8 μg L^{-1} in cow milk sample with a 65 μm PDMS/DVB fiber. Tsoukali et al obtained higher LODs from whole blood and with a 85 μm PA fiber, as for the Malathion (0.36 μg L^{-1} for palm wine sample and 45 μg L^{-1} for whole blood sample) or Parathion methyl (0.01 μg L^{-1} for palm wine sample and 50 μg L^{-1} for whole blood sample). Rodrigues et al obtained higher LOQs with a LOQ of 6.50 μg L^{-1} for Ethion (LOQ of 0.62 μg L^{-1} for optimized method). The developed method offered better performances for those compounds.

3.1.2.1.3 Relative standard deviation

Table 2

Repeatabilities and recoveries of pesticides

No.	Pesticides	Replicate 1 (0.5-2.5 μg L^{-1}) [a]		Replicate 2 (2.5-12.5 μg L^{-1}) [a]		Replicate 3 (5-25 μg L^{-1}) [a]	
		RSD (%) (n = 3)	Relative recovery (%)	RSD (%) (n = 3)	Relative recovery (%)	RSD (%) (n = 3)	Relative recovery (%)
1	Dichlorvos	14.5	116	5.8	95	1	100
2	BHC	10.8	51	11.1	97	3.6	107
3	Hexachlorobenzene	7.9	114	1.4	100	2.5[b]	75[b]
4	Simazine	6.2[d]	102[d]	36.5[e]	88[e]	59.3[f]	100[f]
5	BHC	3.9	80	0.9	102	3.7	103
6	Atrazine	11.2[d]	115[d]	31.8[e]	98[e]	41.7[f]	117[f]
7	Lindane	22.1	73	12.2	100	2.7	103
8	Terbuthylazine	18.7	94	0.7	98	1.1	102
9	Diazinon	14.7[d]	95[d]	11.6	115	6.1	85
10	BHC	22	96	6.9	96	3.1	92
11	Parathion methyl	7.2	110	3.8	99	2.7	102
12	Tolclofos-methyl	15.8	103	15.5	97	5.4	101

13	Alachlor	4	100	4.2	99	6.2	100
14	Heptachlor	7.8	110	3.9	99	0.7	100
15	Pirimidiphos methyl	8.9	113	21.4	95	7.1	101
16	Malathion	4.4[d]	100[d]	5	82	1.4	109
17	Chlorpyrifos	21.9	44	22.1	93	6.6	110
18	Aldrin	7	109	4.3	99	0.3	100
19	Heptachlor epoxide	17.3	100	11.6	101	6.1	93
20	α-Endosulfan	14.1	102	10.3	105	2.9	99
21	Chlordane	19.1	107	12.9	100	18.2	100
22	trans-Nonachlor	40.4	116	37.6[d]	90[d]	13.2	98
23	Prothiofos	18.6	100	20.4	100	6.6	100
24	p,p'-DDE	20.7	113	19.3	92	6.5	102
25	Dieldrin	15	105	15.2	97	4.5	101
26	Endrin	13.5	115	14.2	100	6.5	100
27	β-Endosulfan	20.7	116	23.2	104	9.9	96
28	cis-Nonachlor	36.9	105	31.4[d]	117[d]	11.9	99
29	p,p'-DDD	17.9	110	15.1	95	9.3	102
30	Ethion	22	84	38	105	13.6	102
31	Endrin aldehyde	16.4	72	11.4	103	11.6[d]	100[d]
32	Endosulfan sulfate	10.6	108	11.9	98	11.3[d]	100[d]
33	p,p'-DDT	26.8	120	17.3	99	9.4[d]	100[d]
34	Endrin ketone	9.4	97	15.2	97	12.1[d]	100[d]
35	Methoxychlor	44[c]	109[c]	26.6	90	14.7	102

[a] range of concentrations

[b] at the concentration of 0.5 μg L^{-1}

[c] at the concentration of 1 μg L^{-1}

[d] at the concentration of 100 μg L^{-1}

[e] at the concentration of 500 μg L^{-1}

[f] at the concentration of 1000 μg L^{-1}

As the pesticides were not at the same concentration in the stock solution, spiking was at three levels and for each level the pesticides were not at the same concentration. For the first level, the concentrations were between 0.5 (for chlorpyrifos and pirimiphos methyl for example) and 2.5 μg L^{-1} (for dichlorvos for example), between 2.5 and 12.5 μg L^{-1} for the second level, and between 5 and 25 μg L^{-1} for the final level. Some pesticides were not detected at these concentrations, such as simazine or atrazine, because its LOD were higher than the range of concentrations. Their RSDs and relative recoveries were calculated thanks to higher

concentrations (between 100 and 1000 μg L^{-1}). Some others were not detected at one concentration of the range tested, such as methoxychlor (replicate 1) or trans and cis-nonachlor (replicate 2), their RSDs and relative recoveries were calculated from another concentrations (at 1 μg L^{-1} instead of 2 μg L^{-1} and at 100 μg L^{-1} instead of 5 μg L^{-1}, respectively for methoxychlor, and for trans-nonachlor, and cis-nonachlor).

Atrazine, cis-nonachlor, trans-nonachlor, ethion, methoxychlor, and simazine had RSDs higher than 20% for two replicates. Moreover, for these pesticides the calibration curve was only realized with 3 points, except for ethion (with 4 points), so they were identifiable but not quantifiable for this study.

The RSDs obtained, for the other pesticides, were between 3.9 and 26.8% for BHC and p,p'-DDT, respectively, at 1 ug L^{-1} for the replicate 1, between 0.7 and 23.2% for terbuthylazine and β-endosulfan, respectively, at 5 ug L^{-1} for the replicate 2, and between 0.3 and 18.2% for aldrin (at 20 μg L^{-1}) and chlordane (at 20 μg L^{-1}), respectively, for the replicate 3. The results are shown in Table 2. RSDs were mostly under 20% for replicates 1 and 2, respectively for 23/31 and 25/31 pesticides, and under 10% for replicate 3 for 25/31 pesticides. Little variation of peak areas used to calculate RSDs for low concentrations could have an important effect, so RSDs were lower for concentrations of the replicate 3. The first BHC (RSD of 3.9% for replicate 1, 0.9% for replicate 2, and 3.7% for replicate 3) and parathion methyl (RSD of 7.2% for replicate 1, 3.8% for replicate 2, and 2.7% for replicate 3) were pesticides with the lower RSDs for all replicates.

3.1.2.1.4 Relative recovery

Very good recoveries were obtained for all pesticides at level 3 (75% for hexachlorobenzene and 110% for chlorpyrifos) and level 2 (from 82% for malathion to 115% for diazinon). At level 1, the relative recoveries ranged from 72 to 120% (72% for endrin aldehyde and 120% for

p,p'-DDT at 1 μg L^{-1}, respectively) except for BHC and chlorpyrifos, which showed the applicability of the developed method.

3.1.2.2 Pesticides in palm wine samples

Thirty-two palm wines were analyzed following the optimized HS-SPME-GC/MS method. Seven pesticides (dichlorvos, endrin ketone, parathion methyl, p,p-DDD, p,p-DDE, p,p-DDT, and pirimidiphos methyl) were identified in 10 palm wine samples (AP1, AP2, AR3, BP4, HR4, TP1, TP2, TR1, TR2, and TR3) as presented in Table 3. Pesticides were found in palm wines from the 4 cities, in 3 samples from Abidjan, 1 from Aboisso, 1 from Hiré, and 5 from Toumodi, with concentrations from 0.26 to 164.7 μg L^{-1} for pirimiphos methyl in AP2 and dichlorvos in AR3, respectively. p,p'-DDT was identified in 5 palm wines, in 4 from Toumodi in low concentrations (from 0.503 for TP1 to 0.669 μg L^{-1}). This study is among the first to detect these pesticides in alcoholic beverages.

In AP1, AP2, BP4, HR4, TP1, TP2, TR1, and TR3 palm wine samples, pesticides were quantified at concentrations close to LOQs. EML of pesticides in bunches of grapes are used because in France, the European Maximal Limits (EML) for wine does not exist. Parathion methyl was detected at 0.521 μg L^{-1} in AP1, which is a concentration below the EML, as well as a level below the concentration found in wines from different European countries, such as Spain or Portugal (Table 3). In AR3 and TR2, dichlorvos was detected at 164.7 and 38.4 μg L^{-1}, respectively. As no study has detected this pesticide in alcoholic beverages, results were compared with the concentration of ethion and malathion (organophosphorus pesticides as dichlorvos) in wines from Brazil. Ethion was detected at concentrations between 0.29 and 0.32 μg L^{-1} and malathion at 4.4 μg L^{-1}. Dichlorvos was found at a level above the EML and concentrations found in wines from Brazil (Table 3).

Table 3

Pesticides concentrations in palm wines, European Maximal Limits of pesticides in bunches of grapes and palm oil and comparison with other studies

	European Maximal Limits (ug/kg)		Concentrations (µg L^{-1})												
Pesticides	Bunches of grapes [a]	Palm oil [a]	AP1	AP2	AR3	BP4	HR4	TP1	TP2	TR1	TR2	TR3	Different countries (Brazil, Portugal, Argentina, Chile)	Spain	Brazil
Dichlorvos	10	10			164.7						38.4				
Parathion methyl	10	20	0.521										2.80 [b]	3-4 [c]	
Pirimiphos methyl	10	10		0.26											
p,p'-DDE	50	50				0.645									
p,p'-DDD	50	50						0.609							
p,p'-DDT	50	50					0.575	0.503	0.669		0.671	0.669			
Endrin ketone	-	-								0.529					
Ethion	10	20													0.29-0.32 [d]
Malathion	20	20													4.4 [d]

[a] EU pesticides database

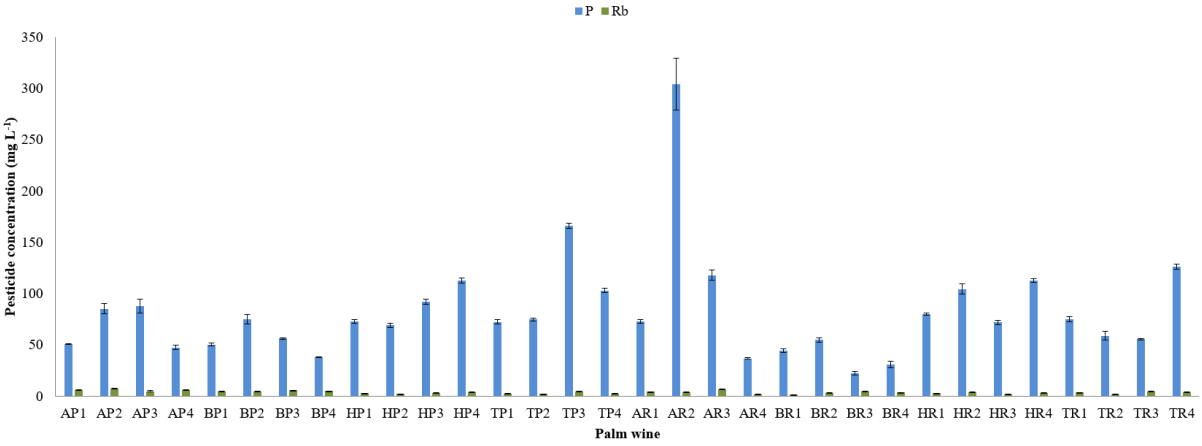
[b] Santiago et al., 2021

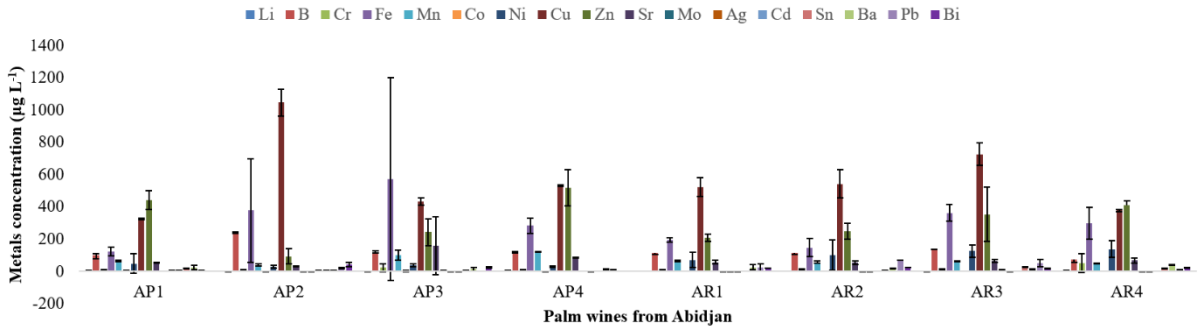
[c] Sala et al., 1997

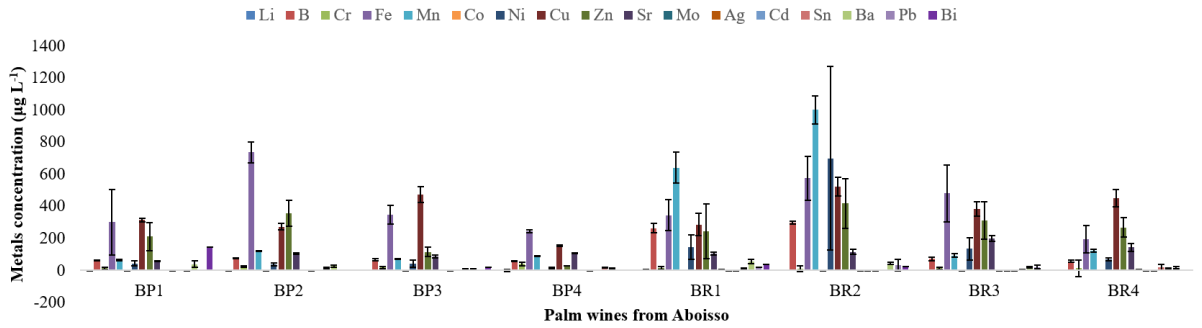
[d] dos Anjos & de Andrade, 2015

3.2 Determination of metals in palm wines

Thirty-two palm wine samples were mineralized and analyzed by ICP-AES and ICP-MS. The results are shown in Figure 2.







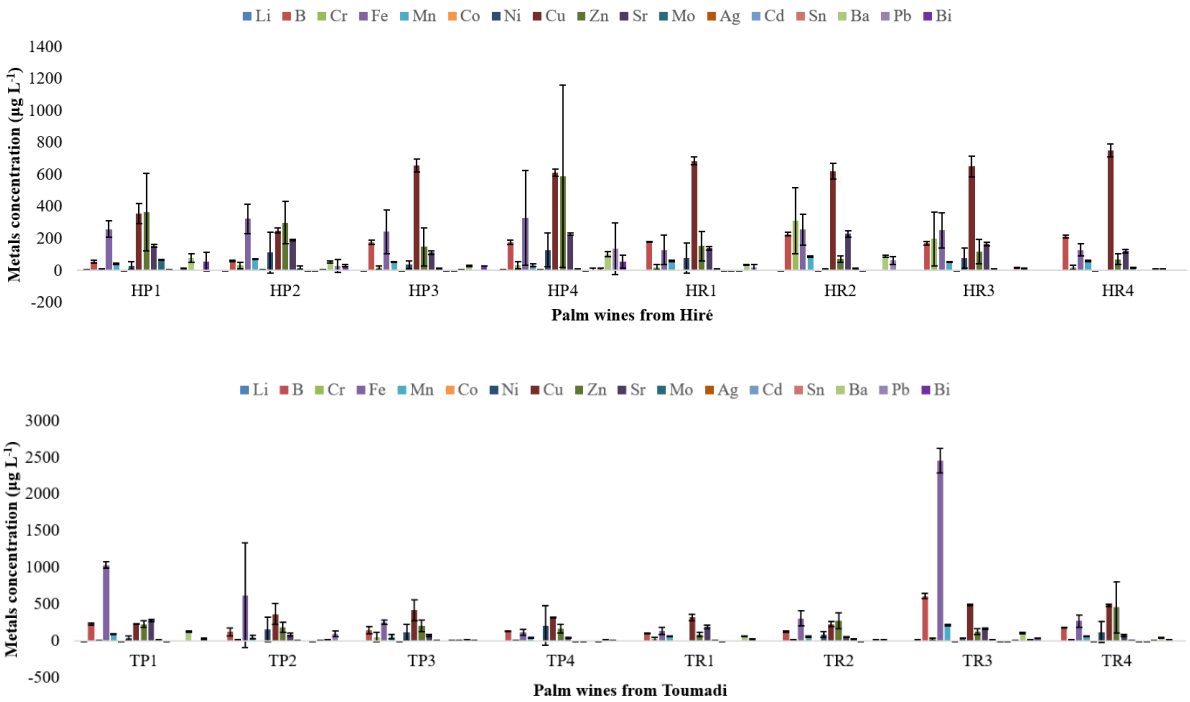


Fig. 2. Metals concentration in 32 palm wine samples, determined by ICP-AES and ICP-MS

The error bars on the graph can be important, because of the heterogeneity of the wine composition. Indeed, when an identical volume is taken, particles can be present, and those being certainly richer in metals, that can have an important role on the concentration of metals.

First, barium, boron, chromium, copper, iron, lead, manganese, phosphorus, rubidium, strontium, and zinc were found in all palm wine samples. The International Organization of Vine and Wine (OIV) recognized maximum limits for only a few elements in wine (Pb, Cd, Cu, Na, Zn, Ag, As, F, Br, F, and B). The levels of the other metals in palm wine, which is composed by 88% of water, can be compared with metal limits of drinking water. The higher concentrations for the most wine samples were found for phosphorus, rubidium, copper and iron, from 22.2 mg L^{-1} (BR3) to 303.9 mg L^{-1} (AR2) for phosphorus, from 1.5 mg L^{-1} (BR1) to 7.6 mg L^{-1} (AP2) for rubidium, from 155.6 (BP4) to 1046.9 µg L^{-1} (AP2, this concentration was above the OIV maximal limit of 1000 µg L^{-1}) for copper and from 116.4 (TP4) to 2453.5 µg L^{-1} (TR3) for iron. Manganese was mostly identified in samples from Aboisso, mainly in BR1

(641.6 μg L^{-1}) and BR2 (1001.3 μg L^{-1}) palm wines, at levels above the European maximal limits for drinking water.

Then, six metals (cadmium, chromium, copper, iron, manganese, and nickel) were detected in different samples at levels above the European maximal limits for drinking water or above the OIV maximal limits for wine. Cadmium was detected in TP3 (13.8 μg L^{-1}) at level above limits of 10 μg L^{-1}, and chromium in TP3 (51.4 μg L^{-1}), AR4 (52.2 μg L^{-1}), HR2 (313.4 μg L^{-1}), and HR3 (197.9 μg L^{-1}) at level above limits of 50 μg L^{-1}.

Iron was at level above limits of 200 μg L^{-1} in 24 samples (AP2, AP3, AP4, AR1, AR2, AR3, AR4, BP1, BP2, BP3, BP4, BR1, BR2, BR3, BR4, HP1, HP2, HP3, HP4, HR1, HR2, HR3 ,HR4, TP1, TP2, TP3, TP4, TR1, TR2, TR3, and TR4), from 242.2 (HP3) to 2453.5 μg L^{-1} (TR3), and nickel at level of 20 μg L^{-1} in 28 samples too (AP1, AP2, AP3, AP4, AR1, AR2, AR3, AR4, BP1, BP2, BP3, BR1, BR2, BR3, BR4, HP1, HP2, HP3, HP4, HR1, HR2, HR3, HR4, TP1, TP2, TP3, TP4, TR1, TR2, TR3, and TR4), from 28.9 (AP4) to 699.8 μg L^{-1} (BR2).

Zinc, which was detected at a range of concentrations between 28.6 and 589.9 μg L^{-1}, was also found in wines from different European countries, such as Italy or France (Table 4), at similar and higher levels (for example, between 289 and 967 μg L^{-1} for Italian wines). As for Italian and French wines, zinc was not detected at levels above the OIV maximal limits for wine. Moreover, cadmium was detected in one sample (TP3) at concentration above the OIV maximal limit of 10 μg L^{-1}. However, its concentration in Italian and French wines was not at levels above the limits.

Metals, like copper, iron, and zinc, are essential for human at low concentrations. However, at important concentrations, they can pose a real danger. For example, drinking water contaminated by cadmium and lead can cause renal failure or chromium and nickel can induce hair loss (Singh Sankhla et al., 2016).

Finally, the palm wine TP3 from Toumodi was the most polluted sample with metals at levels above European and OIV maximal limits (cadmium, chromium, iron, manganese and nickel), given Table 4.

Table 4

KED, or STD mode, LODs and LOQs of metals in palm wines, European and OIV Maximal Limits of metal in drinking water and wine, and comparison with other studies

Metals	Mode	LOQ (µg L^{-1})	LOD (µg L^{-1})	European Maximal Limits in drinking water (µg L^{-1})	OIV Maximal Limits (µg L^{-1})	Concentrations in French wines (mg L^{-1}) [a]	Concentrations in Italian wines (mg L^{-1}) [a]	Concentrations in Italian wines (µg L^{-1}) [b]	This study (µg L^{-1}) or (mg L^{-1}) [c]
Barium	KED	1.5	0.45	-	-				3.65-132.4
Bismuth	STD	17	5.1	-	-				18.5-146.3
Boron	STD	4	1.2	1500	80000			1995-9489	55.7-614.4
Cadmium	STD	0.75	0.23	5	10	ND–0.0002	0.0012–0.0016	0.17-3.7	0.36-13.8
Chromium	KED	5	1.5	50	-	0.006-0.09	0.02-0.05		5.86-313.4
Cobalt	STD	0.5	0.15	-	-	0.004-0.005	0.003-0.006		0.52-7.35
Copper	KED	3	0.9	2000	1000	ND–0.48	0.001–1.34	14-456	155.6-1046.9
Iron	KED	16.5	4.95	200	-	0.81–2.51	1.35–27.8		116.4-2453.5
Lead	KED	8.5	2.5	10	150	0.006–0.023	0.01–0.35	3-59	0.38-135.4
Lithium	STD	0.25	0.08	-	-				0.33-18.0
Manganese	KED	1	0.3	50	-	0.63–0.96	0.67–2.5		33.2-1001.3
Molybdenum	KED	1.3	0.38	-	-				1.36-69.0
Nickel	KED	9.3	2.9	20	-	ND–0.052	0.015–0.21		12.9-699.8
Phosphorus	-	450	140	-	-				22.2-303.8 [c]

Rubidium	-	80	20	-	-				1.52-7.62 [c]
Silver	KED	0.5	0.15	-	-				0.51-2.74
Strontium	KED	2	0.6	-	-				33.2-281.7
Tin	KED	1.3	0.38	-	-				2.18-24.8
Zinc	KED	12	3.6	-	5000	0.44–0.74	0.135–4.8	289-967	28.6-589.9

[a] Płotka-Wasylka et al., 2018

[b] Caridi et al., 2019

4. Conclusion

In this study, the concentration of pesticides and metals in palm wines from Ivory Coast using HS-SPME/GC-MS and ICP-AES/MS were determined. SPME conditions (equilibrium time, extraction time and temperature, stirring, and salinity) were optimized thanks to an experimental design with 45 trials. The developed method used a DVB/C-WR/PDMS fiber and the palm wine samples were equilibrated for 11.25 min and extracted for 50 min under continuous stirring (437.5 rpm) at 52.5°C. The method was validated in terms of linearity, repeatability, LOD, LOQ, and accuracy, and allowed the identification of 35 pesticides and the quantification of 29 in 32 palm wine samples. Additionally, 7 pesticides were identified but dichlorvos was the only one identified in 2 samples at levels above the European maximal limits.

In a second step, ICP-AES and ICP-MS were used to study the presence of 19 metals in palm wine samples. Barium, boron, chromium, copper, iron, lead, manganese, rubidium, strontium, and zinc explored were identified in all samples of palm wine. Moreover, 6 metals (cadmium, chromium, copper, iron, manganese, and nickel) were detected in different samples at levels above the European maximal limits for drinking water or above the OIV maximal limits for wine.

Finally, pesticides (dichlorvos, endrin ketone, parathion methyl, p,p-DDD, p,p-DDE, p,p-DDT, and pirimidiphos methyl) were found in palm wines from the 4 cities, in 3 samples from Abidjan,

1 from Aboisso, 1 from Hiré, and 5 from Toumodi. In addition, one of the palm wine samples from Toumodi was the most polluted sample with metals (cadmium, chromium, iron, manganese and nickel) at levels above European or OIV maximal limits.

Maximal limits for metals have been only defined for boron, cadmium, copper, lead and zinc. As shown in this article, samples may contain pesticides and metals in high concentrations. This beverage is largely consumed by local population. It would be important to develop more studies on the composition of palm wine and maximal limits especially for pesticides in wines, in order to be aware of the potential danger of its consumption.

List of abbreviations

PA: polyacrylate

BHC: Hexachlorocyclohexane

Carbon WR: Carbon Wide Range

DVB: Divinylbenzene

EML: European Maximal Limits

GC: Gas Chromatography

GC-MS: Gas Chromatography coupled with Mass Spectrometry

HS-SPME: Headspace Solid-Phase Microextraction

ICP-AES: Inductively Coupled Plasma - Atomic Emission Spectrometry

ICP-MS: Inductively Coupled Plasma - Mass Spectrometry

KED: Kinetic Energy Discrimination mode

LOD: limit of detection

Log Kow: octanol-water partition coefficient

LOQ: limit of quantification

MS: mass spectrometry

OCPs: OrganoChloride Pesticides

OIV: International Organization of Vine and Wine

OPPs: OrganoPhosphorus Pesticide

PDMS: Polydimethylsiloxane

p,p’-DDD: Dichlorodiphenyldichloroethane

p,p’-DDE: Dichlorodiphenyldichloroethylene

p,p’-DDT Dichlorodiphenyltrichloroethane

RSD: relative standard deviation

SIM: Single Ion Monitoring

STD: Standard mode

SPME: Solid-Phase Microextraction

Authors' contributions

Juliette Vievard wrote the paper, performed the analysis, collected the data

Theodore N'Dede Djeni wrote the paper, gave samples

Christine Devouge-Boyer contributed to data and analysis

Monica Arellano Gisel Sanchez wrote the paper

Aké Francine collected the samples

Tiemele Laurent Simon Amoikon wrote the paper, gave samples

Aminata Nadjoua Coulibaly, wrote the paper, collected the samples

Mélanie Mignot oversight the study, reviewed the paper

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