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Determination of cadmium and lead in beverages after leaching from pewter cups using graphite furnace atomic absorption spectrometry

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ABSTRACT

Two simple methods have been developed to determine cadmium and lead in different kinds of beverages and vinegar leached from pewter cups produced in Brazil. Leaching experiments have been carried out with different solutions: beer, sugar cane spirit, red and white wine, vinegar and a 3% acetic acid solution. The solutions were kept in cups with and without solder for 24 h. Lead and cadmium have been determined using graphite furnace atomic absorption spectrometry with deuterium background correction. The limits of detection were 0.05 and 1.4 $\mu g\,L^{-1}$, and the characteristic mass was 1.0 pg and 19 pg for Cd and Pb, respectively. With the developed methods it was possible to determine accurately cadmium and lead by direct analysis in these liquids and to evaluate the leaching of these metals from pewter cups. The results presented in this work show that pewter cups are not cadmium- and lead-free; this point goes against the manufacturers' declaration that their products are lead-free.

1. Introduction

Unalloyed tin is too soft to be used for kitchenware, tableware, drinking cups, etc.; hence a small percentage of hardening agents, such as copper, bismuth, antimony and lead are usually added, either alone or in combination, to make it more durable. These tin alloys are known as pewter. Today the composition of pewter for domestic use is rigidly controlled, based on British and European standards, specifying a minimum of 90% tin with the balance being made up of copper, antimony and perhaps some bismuth. The main difference from the seventeenth and eighteenth century ordinances is that the addition of lead is no longer permitted, with the maximum allowed level being 0.5% – in practice usually far less, so that lead should be present as a trace element only [1].

Pewter was part of everyday's life until the 19th century. Eating, drinking, celebrating, lighting rooms and taking communion all required long-lasting, affordable objects [1]. Nowadays pewter is enjoying a Renaissance worldwide, and its use is growing every year; both, consumers and craftsmen, have rediscovered the beauty and practical function of fine pewter. Pewter production is a very important source of income for São João del-Rei, a Brazilian city situated in the state of Minas Gerais, which is one of the major production centers of pewter artifacts in Latin America [2].

It is well known that heavy metals, such as Cd and Pb, are toxic. The leaching of these elements from pewter cups hence could represent a health hazard. Krachler and Shotyk [3] reported the leaching of relatively high concentrations of Tl and Sb from pocket flasks made of pewter. Considering the increasing use of pewter kitchenware in some regions of Brazil, it is of great importance to evaluate the leaching of potentially toxic metals from these utensils. In this work, leaching experiments have been carried out with pewter cups produced in Brazil nowadays, using beer, sugar cane spirit, red and white wine, vinegar and 3% acetic acid as test solutions.

Graphite furnace atomic absorption spectrometry (GF AAS) was the technique chosen for the determination of cadmium and lead, a technique with high sensitivity and tolerance to inorganic and organic matrices, which should make possible a direct determination of these analytes in the selected liquids. The literature is quite limited regarding the direct determination of metals in beverages by GF AAS. Most publications about the determination of metals in wine involve some kind of sample preparation. Mihaela et al. [4] used microwave-assisted mineralization of red and white wine for the determination of Pb by GF AAS; the authors reported an average

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recovery of 67%, which indicates some analyte loss during mineralization or some interference in the determination. Jos et al. [5] analyzed different elements in sparkling wines employing a degasification step and a digestion with H_2O_2 and H_2SO_4. Moreno et al. [6] used a dry ashing procedure at 450 °C, followed by dilution with HNO_3 to determine Pb and Ni in red wine samples by GF AAS. Others used a simple dilution with nitric acid as sample preparation [7–10]. Capelo et al. [11] developed a procedure for metal extraction from must using focused ultrasound treatment with HNO_3 and H_2O_2 and observed that using this procedure microwave-assisted digestion was not necessary. More recently, the direct determination of cadmium [12], lead [13] and the simultaneous determination of cadmium, lead, copper and arsenic [14] in wine samples were reported using palladium or a mixture of palladium and magnesium nitrates (Pd–Mg) as chemical modifier. All authors found a good correlation between the values obtained by direct determination and by acid digestion. Husáková et al. [15] reported the direct determination of arsenic in beer by GF AAS using aqueous standard solutions for calibration and deuterium background correction; the accuracy of the method was confirmed by comparison with the results obtained with microwave-assisted digestion and inductively coupled plasma mass spectrometry (ICP-MS). Caldas et al. [16–18] determined copper, arsenic and lead in sugar cane spirits directly without any sample pretreatment and compared the results obtained by GF AAS with those found by ICP-MS. Ndung'u et al. [19] observed that the precision for Pb determination in vinegar improved when using digestion instead of direct analysis. The authors also recommended adjusting the graphite furnace temperature program taking into consideration the presence of volatile organo-lead compounds. Cocchi et al. [20] reported low recoveries for Cd and Pb, using dry ashing for sample preparation. de Oliveira et al. [21,22] reported the direct determination of lead in vinegar by GF AAS, using the combination of a permanent modifier and Pd–Mg as conventional modifier. The comparative results and recovery values of spiked samples indicated that no sample treatment was necessary to accurately determine Pb in vinegar samples.

The goal of this work was to develop a method for the direct determination of cadmium and lead in beer, sugar cane spirit, red and white wine, vinegar and a 3% acetic acid solution, using GF AAS, and to evaluate the leaching of these metals from pewter cups to the different liquids. Cups from three manufacturers from Minas Gerais, Brazil, with and without solder, have been investigated.

2. Materials and methods

2.1. Instrumentation

All measurements have been carried out using a Model AAS 5 EA atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with deuterium background correction and a transversely heated graphite tube atomizer. Hollow cathode lamps for cadmium and lead (NARVA, GLE, Berlin, Germany) were used as radiation sources, both with a lamp current of 3.5 mA. The analytical wavelengths used were 228.8 nm for cadmium and 283.3 nm for lead with a spectral band pass of 0.8 nm.

Pyrolytic graphite coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025) were used for all measurements. An MPE 5 furnace autosampler (Analytik Jena) was used for introduction of samples and standards into the graphite furnace. The spectrometer was interfaced to an IBM PC/AT compatible computer. Integrated absorbance (peak area) was used exclusively for signal evaluation and quantification. The optimized parameters for the graphite furnace temperature program for both analytes are given in Table 1. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as purge and protective gas.

Table 1
Graphite furnace temperature program for the determination of cadmium and lead in beverages and vinegar samples; purge gas (argon) flow rate: 2 L min^{-1} in all stages, except during atomization, when the gas flow was interrupted.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)
Drying	100	15	40
Drying	120	50	40
Pyrolysis	700[a]; 900[b]	50	30
Atomization	1300[a]; 2000[b]	3000	6
Cleaning	2300	1000	4

[a] Cd.
[b] Pb.

A digester block Model 324 A 242 (Quimis, Brazil) was used for digesting the samples.

2.2. Reagents and solutions

Analytical grade reagents were used exclusively. Distilled, deionized water with a specific resistivity of 18 MΩ cm from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for the preparation of standards and modifier solution. All containers and glassware were soaked in 1.4 mol L^{-1} nitric acid for at least 24 h and rinsed three times with water before use. Nitric acid (Merck, Darmstadt, Germany) was further purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany).

Stock standard solutions for cadmium and lead (1000 mg L^{-1} in 0.014 mol L^{-1} nitric acid) were prepared from Titrisol concentrates (Merck). The working standards were prepared by serial dilution of the stock solutions with 0.014 mol L^{-1} nitric acid. A mixture of 1000 mg L^{-1} Pd + 600 mg L^{-1} Mg (Pd and Mg as nitrates from Merck) was used as the chemical modifier.

For the measurements, 20 μL of sample was injected into the furnace with 10 μL of the chemical modifier solution, corresponding to a mass of 10 μg Pd and 6 μg Mg, and submitted to the heating program shown in Table 1. The standard calibration technique with aqueous standard solutions was used for all determinations.

2.3. Samples and leaching procedure

Sugar cane spirit, beer, red and white wine, and vinegar, acquired in a local supermarket, and a 3% acetic acid solution prepared from glacial acetic acid (F. Maia, Brazil) were used to evaluate cadmium and lead leaching from pewter cups. The pewter cups of three different manufacturers (called A, B and C) were evaluated, originating from the same city, São João del Rei, MG, Brazil. Six cups with a volume of 30–50 mL without solder and six cups with a volume of 250–300 mL with solder have been purchased from each of the manufacturers to investigate the influence of the solder on the metal migration. The cups were identified with numbers from 1 to 6, each number corresponds to a solution, for example, cup A1 is from manufacturer A and was used for acetic acid solution. Before the leaching experiments the cups were washed with deionized water. A volume of 10 mL for cups without solder, and of 150 mL for cups with solder, respectively, of each solution was put into the cups and left in contact at room temperature for 24 h. Then the solutions were transferred to polyethylene flasks and stored in a refrigerator until the analysis was carried out.

To assess the accuracy of the proposed method for the direct determination of cadmium and lead in different kinds of beverages and vinegar, the samples from one leaching experiment – manufacturer C with solder – were submitted to an acid digestion. The digestion procedure employed was the same as described by Ferreira et al. [12]: A volume of 5 mL of each sample was digested in a digester block with the addition of 10 drops of concentrated nitric

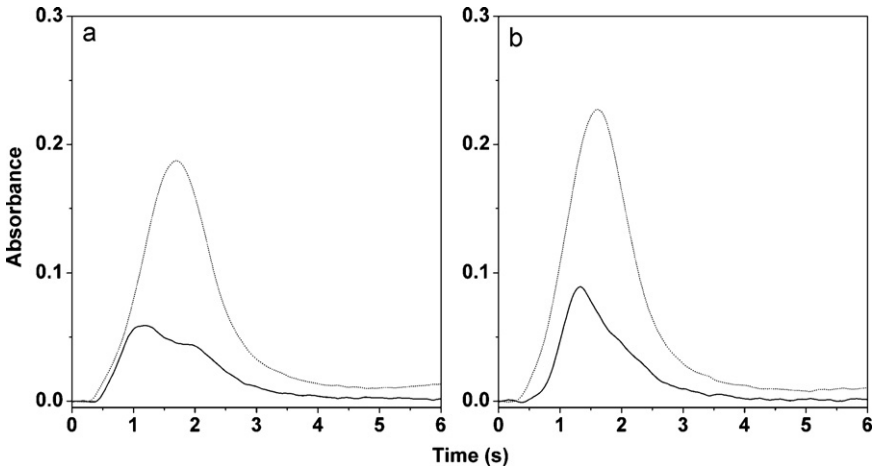

Fig. 1. Peak profiles for cadmium in 20 μL of wine sample with (**a**) 5 μL, and (**b**) 10 μL of Pd-Mg modifier solution; solid line AA and dotted line BG; T_{pyr} = 600 °C and T_{at} = 1500 °C.

acid and 2 mL of 30% (v/v) hydrogen peroxide (Merck). The mixture was heated at 150 °C under reflux for 2 h using a digester system with a "cold finger" [23]. The residue was diluted to 10 mL with deionized water. All samples were digested in triplicate.

3. Results and discussion

3.1. Modifiers and graphite furnace temperature program

In GF AAS the temperature program is used to separate the analyte from the concomitants in situ prior to the atomization stage and the use of chemical modifiers is common practice in order to facilitate the removal of the matrix without loss of volatile analytes such as cadmium and lead [24]. Our group has investigated different chemical modifiers for the direct determination of lead [13] in wine samples. It was found that permanent chemical modifiers could not stabilize cadmium and lead efficiently in wine samples. Moreover, when iridium was used as the permanent modifier, a double peak was observed for lead in wine samples, similar to the signal obtained without modifier. Based on these results, the use of permanent modifiers was not considered in this work.

The mixed palladium and magnesium nitrates (Pd–Mg) modifier [25] added in solution was therefore investigated, and the volume of modifier necessary to stabilize cadmium and lead in the investigated samples was optimized. Five, 10 and 15 μL of modifier solution was added to cadmium and lead aqueous standard solutions and a wine sample from the leaching experiment with a cup without solder from manufacturer C. The integrated absorbance signal for cadmium did not change significantly with increasing modifier volume; however, the peak profile for the wine sample improved considerably when the volume of the modifier was increased from 5 to 10 μL, as shown in Fig. 1. With 5 μL of modifier solution kind of a double peak appeared, as shown in Fig. 1a, which was not observed when 10 or 15 μL of modifier solution was employed; the shape of the signals with 10 and 15 μL of modifier solution was more uniform and very similar. Based on this, a volume of 10 μL of 0.1% Pd + 0.06% Mg solution, corresponding to 10 μg Pd + 6 μg Mg, was chosen for the determination of cadmium in all further experiments.

The integrated absorbance for lead in aqueous solution also did not change significantly when 5, 10 or 15 μL of modifier solution was used, but the integrated absorbance signal for the wine sample increased about 20% when the volume of the modifier solution was increased from 5 to 10 μL. Fig. 2 shows that the peak shapes for lead in the wine sample are very similar with different volumes of chemical modifier added. Since the increase in sensitivity from 10 μL to 15 μL of modifier solution was not significant, a volume of 10 μL of modifier solution was chosen for the determination of lead in all further experiments.

Pyrolysis curves have been established for 3% acetic acid solution, beer, sugar cane spirit, red and white wine and vinegar

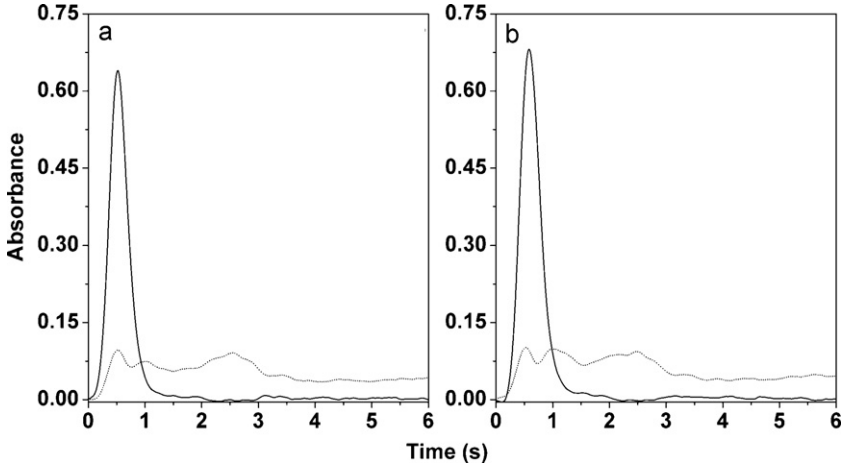

Fig. 2. Peak profiles for lead in 20 μL of wine sample with (**a**) 5 μL, and (**b**) 10 μL of Pd-Mg modifier solution; solid line AA; dotted line BG; T_{pyr} = 900 °C and T_{at} = 2000 °C.

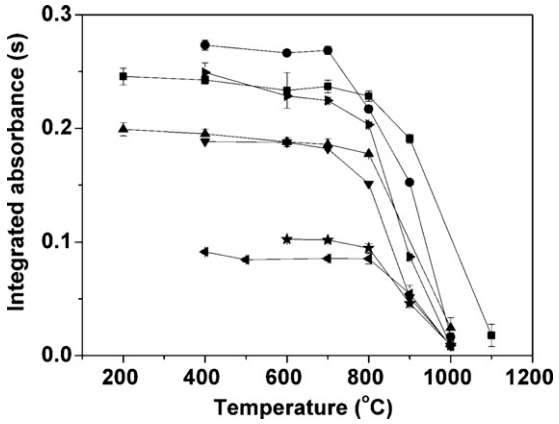

Fig. 3. Pyrolysis curves for cadmium using 20 μL of aqueous standard solution or leached samples and 10 μg Pd + 6 μg Mg as chemical modifier. (■) 100 pg of Cd standard; (⋆) beer; (●) White wine; (►) red wine; (◄) sugar cane spirit; (▼) vinegar; (▲) 3% acetic acid; T_{at} = 1500 °C.

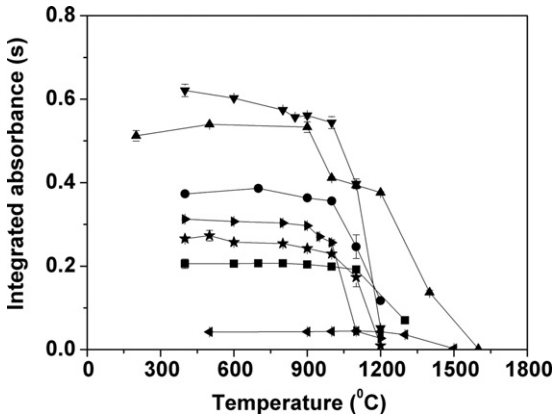

Fig. 4. Pyrolysis curves for lead using 20 μL of aqueous standard solution or samples and 10 μg Pd + 6 μg Mg as chemical modifier. (■) 1.0 ng of lead aqueous standard; (⋆) beer; (●) white wine; (►) red wine; (◄) sugar cane spirit; (▼) vinegar; (▲) 3% acetic acid. T_{at} = 2000 °C.

(leached in cups without solder from manufacturer C) using the optimized volume of 10 μL of the Pd–Mg modifier solution and employing atomization temperatures of 1500 °C for cadmium and 2000 °C for lead. The curves for cadmium are shown in Fig. 3. Due to the high background absorption for beer, red and white wine, vinegar and sugar cane spirit at the cadmium line, measurements were only possible when pyrolysis temperatures of 400 °C or higher were used. For the aqueous standard and 3% acetic acid sample it was possible to measure the analyte signal starting from a pyrolysis temperature of 200 °C. The maximum pyrolysis temperature that could be used for the wine and vinegar samples was 700 °C. This temperature has been chosen for all further experiments, although a somewhat higher temperature of 800 °C could have been used for the other samples. Nevertheless, a pyrolysis temperature of 700 °C is sufficient to reduce the background absorption to a level that could be handled without problems by the deuterium background correction system.

The pyrolysis curves for lead in the various samples are shown in Fig. 4. The maximum pyrolysis temperature that could be used for red wine and 3% acetic acid was 900 °C. For vinegar the signal decreased about 8% between 400 and 900 °C pyrolysis temperature. In order to standardize the experimental conditions for the determination of lead, a pyrolysis temperature of 900 °C was chosen for all future experiments. This pyrolysis temperature allowed removal of the majority of the sample matrix prior to the atomization stage, resulting in low background levels and suitable precision.

After the amount of modifier and the pyrolysis temperatures had been defined, the atomization temperatures had to be optimized. For cadmium atomization curves have been established for an aqueous standard and a vinegar sample. The highest integrated

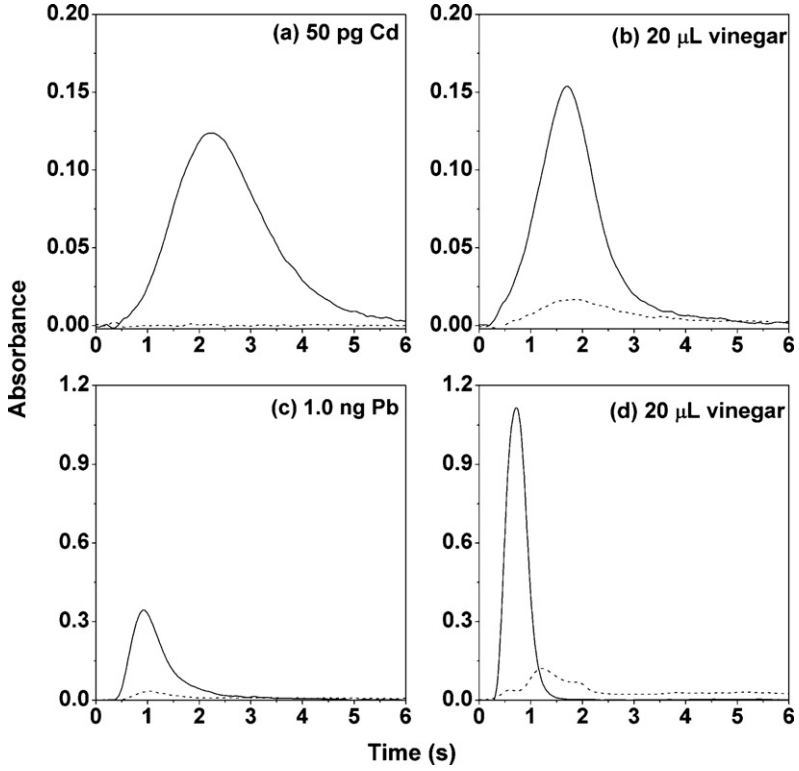

Fig. 5. Absorbance signals for (**a**, **b**) cadmium and (**c**, **d**) lead; solid line AA; dotted line BG. Temperature program as in Table 1; chemical modifier: 10 μg Pd + 6 μg Mg.

Table 2
Figures of merit for the determination of cadmium and lead in beverage and vinegar samples.

	Cadmium	Lead
Linear regression	$A_{int} = 0.0291 + 0.0037m$ (pg)	$A_{int} = 0.0271 + 0.1968m$ (ng)
Correlation coefficient	0.9988	0.9987
LOD ($\mu g L^{-1}$)	0.05	1.4
LOQ ($\mu g L^{-1}$)	0.18	4.5
m_0 (pg)	1.0	19

absorbance values were obtained at 1300 °C for both, standard and sample; hence this atomization temperature has been adopted for all further measurements.

The atomization curves for lead were established for an aqueous standard and a red wine sample. It was observed that lead in an aqueous standard behaved significantly different from lead in wine; the integrated absorbance for the standard increased to a maximum at 2000 °C, whereas for the wine sample essentially the same integrated absorbance was obtained for atomization temperatures between 1400 and 2000 °C. This phenomenon was observed already in a previous work of our group [13]. Based in these results, an atomization temperature of 2000 °C was used in all future experiments. The peak profiles for sample and aqueous standard for both analytes are shown in Fig. 5. Although the peak profiles were generally broader for the aqueous standard, peak shapes for standard and sample were similar for both analytes, and integration over the peak area removed the minor differences. In addition, background signals were negligible, demonstrating the efficient removal of the vinegar matrix prior to the atomization stage.

3.2. Figures of merit

Figures of merit obtained for cadmium and lead are shown in Table 2. Calibration curves were established using a blank and four standard solutions in the concentration range of 2.5–10 $\mu g L^{-1}$ Cd (25–100 pg Cd), and of 20–200 $\mu g L^{-1}$ Pb (0.2–2.0 ng Pb). The limits of detection (LOD) and quantification (LOQ) were calculated as $3\sigma/S$ and $10\sigma/S$, where σ is the standard deviation of ten measurements of the blank solution and S is the slope of analytical curve; they were calculated for 20 μL of sample, the volume injected into the graphite furnace. The characteristic mass (m_0) and LOD obtained are in agreement with the values reported in literature for the determination of cadmium and lead in wine samples [12,14]. The LOQs are comfortably lower than the maximum levels of 500 $\mu g L^{-1}$ for cadmium and lead in alcoholic beverages, established by Brazilian regulations [26]. The Compliance Manual from the Food and Drug Administration (FDA) of the United States also limits the quantities of extractable cadmium and lead from ceramic tableware to acid food at 500 $\mu g L^{-1}$ [27].

Due to the lack of certified reference materials for wine, beer, sugar cane spirits, vinegar, etc., the accuracy of the method was established by comparing the results obtained with the proposed method for one set of leaching experiments (cups with solder from manufacturer C) with those found after sample mineralization using acid digestion, as described in Section 2.3, followed by the determination with GF AAS. The acetic acid solution was not submitted to the acid digestion procedure because it was already in an aqueous medium. The results are given in Table 3; all values were compared using a paired Student's t-test and there was no significant difference in the results for undigested and digested samples at the 95% confidence interval. Comparing the results for each element and sample individually, the result for cadmium in red wine without and with digestion were found to be significantly different; however, this difference was not considered important, as the values were more than two orders of magnitude lower than the limit set by legislation. This shows that the proposed method is providing accurate results for cadmium and lead, although it is very simple and uses aqueous standards for calibration.

3.3. Application

The proposed method has been applied for the determination of cadmium and lead in samples of 3% (v/v) acetic acid, beer, sugar cane spirit, wines and vinegar after having been left in pewter cups with and without solder for 24 h. The products of three different manufacturers of pewter were compared. The results are shown in Tables 4 and 5. Comparing the results, it appears that beer and sugar cane spirit are leaching out the lowest concentrations of Cd and Pb, although there are obvious differences for some of the pewter manufacturers. For red and white wine no significant difference could be found for the amount of cadmium extracted from cups without or with solder, whereas significantly more lead has been

Table 3
Comparison between of the values obtained for cadmium and lead by direct sampling and after acid digestion procedure for samples leached for 24 h in cups with solder from manufacturer C. Values are in $\mu g L^{-1}$; $n = 3$.

Sample	Cadmium		Lead	
	Direct sampling	Mineralized samples	Direct sampling	Mineralized samples
Acetic acid 3%	2.23 ± 0.05	–	53.9 ± 0.5	–
Beer	<LOQ	<LOQ	52.4 ± 0.5	67.3 ± 2.8
Sugar cane spirit	<LOQ	<LOQ	<LOQ	<LOQ
White wine	1.32 ± 0.05	1.53 ± 0.11	160 ± 2.0	151 ± 1.4
Red wine	2.63 ± 0.09	1.99 ± 0.06	114 ± 2.6	113 ± 13
Vinegar	1.20 ± 0.01	1.10 ± 0.05	336 ± 4.2	344 ± 2.9

Table 4
Cadmium concentration in samples before leaching and after leaching for 24 h in cups with and without solder from manufacturers A, B and C. Values are in $\mu g L^{-1}$ and $n = 3$.

Manufacturer	Before leaching	Cups without solder			Cups with solder		
		A	B	C	A	B	C
Acetic acid 3%	<LOQ	8.62 ± 0.23	1.70 ± 0.06	2.43 ± 0.01	0.63 ± 0.001	0.23 ± 0.01	2.23 ± 0.05
Beer	<LOQ	<LOQ	<LOQ	1.00 ± 0.04	0.50 ± 0.002	<LOQ	<LOQ
Sugar cane spirit	<LOQ	<LOQ	<LOQ	0.87 ± 0.01	<LOQ	<LOQ	<LOQ
White wine	0.38 ± 0.01	0.70 ± 0.04	0.60 ± 0.03	3.22 ± 0.11	1.00 ± 0.006	0.95 ± 0.03	1.32 ± 0.05
Red wine	1.12 ± 0.05	2.59 ± 0.09	1.96 ± 0.06	3.91 ± 0.12	1.17 ± 0.007	2.33 ± 0.08	2.63 ± 0.09
Vinegar	<LOQ	0.50 ± 0.02	0.45 ± 0.01	1.74 ± 0.01	0.32 ± 0.02	0.21 ± 0.01	1.20 ± 0.01

Table 5
Lead concentration in samples after leaching for 24 h in cups with and without solder from manufacturer A, B and C. Values are in $\mu g\,L^{-1}$ and $n = 3$.

Manufacturer	Before leaching	Cups without solder			Cups with solder		
		A	B	C	A	B	C
Acetic acid 3%	<LOQ	797 ± 14	1003 ± 1.3	1131 ± 15	342 ± 4.7	344 ± 0.4	53.9 ± 0.5
Beer	<LOQ	<LOQ	<LOQ	49.5 ± 1.6	24.8 ± 0.12	5.39 ± 0.46	52.4 ± 0.5
Sugar cane spirit	<LOQ	6.07 ± 0.37	<LOQ	7.65 ± 0.12	24.8 ± 0.4	<LOQ	<LOQ
White wine	11.7 ± 0.45	19.9 ± 0.6	16.2 ± 0.4	68.7 ± 2.9	94.2 ± 3.4	115 ± 1.1	160 ± 2.0
Red wine	8.04 ± 0.26	19.9 ± 0.3	72.3 ± 2.1	63.3 ± 0.6	25.9 ± 0.9	281 ± 3.6	114 ± 2.6
Vinegar	7.09 ± 0.19	83.1 ± 0.9	34.3 ± 0.9	105 ± 0.5	8.66 ± 0.3	292 ± 3.1	336 ± 4.2

extracted from cups with solder. Another interesting comparison is that between 3% acetic acid and vinegar; with only one exception, the extraction of Cd and particularly of Pb are much higher for acetic acid than that due to vinegar, although the acid concentration is comparable. The lead amount leached by acetic acid from cups without solder are higher than the limit allowed by Brazilian and FDA regulations, which is 500 $\mu g\,L^{-1}$.

4. Conclusion

Two simple methods to determine cadmium and lead in different kind of beverages and vinegar have been developed. Using these methods it was possible to determine accurately cadmium and lead by direct analysis in different liquids and to evaluate the leaching of these metals from pewter cups. The results presented in this work showed that pewter cups are not cadmium- and lead-free; this point goes against the manufacturers' declaration that their products are lead-free.

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