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Evaluation of recycle and reuse of nitric acid from sample digests by sub-boiling distillation

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ABSTRACT

An analytical procedure was developed for recovering HNO_3 from sample digests generated after microwave-assisted digestion procedures. Rice and bovine muscle digests were mixed with technical grade HNO_3 in different proportions and submitted to distillation using a sub-boiling apparatus. Arsenic, Ca, Cu, Fe, Mg, Mn, Na, P, and Zn were determined before and after distillation of solutions, revealing that the procedure was efficient for removal of most contaminants. It was observed that the percentage of contaminant removal ranged from 98.1 to 99.8% for all evaluated procedures. Two certified reference materials, NIST 8414 (Bovine Muscle) and NIST 1570a (Spinach Leaves), were digested using recovered acid from rice digests by sub-boiling distillation and all analyte recoveries ranged from 73 to 106%. Digests obtained from NIST 8414 were also submitted to the same sub-boiling distillation procedure and As, Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, P, Pb, Se, Sr, V, and Zn were determined. Sub-boiling distillation of sample digests is a promising procedure for adopting green chemistry principles, such as minimizing the quantity of residues generated and recycling of reagents.

1. Introduction

Generally in microwave-assisted digestion, acids are used in larger volumes than samples, so their purities are a key aspect to achieve low analytical blanks. Therefore, the quality of reagents is extremely important for trace element analysis because sample contamination may occur by different factors which are commonly found in chemical laboratories, such as apparatus, reagents, flasks and the analyst her/himself [1]. Some strategies were developed in order to produce ultrapure reagents such as conventional distillation, isothermal distillation and sub-boiling distillation. Conventional distillation is applied for the purification of most solvents; however, in most cases, there is no control of the temperature. Thus, there might be the generation of aerosols, which leads to the formation of droplets of unpurified liquids that may be carried through the distillator, hence contaminating the distillate [2]. Vaporization without excessive boiling may also prevent the deposit of contaminants inside the distillation still, which may be contained in acid vapors and contaminate the distillate [3].

Isothermal distillation was developed to produce high purity reagents from chemicals with a high vapor pressure at room temperature, such as hydrochloric acid. If the acid and pure water are placed on a sealed chamber, the acid vapor will be absorbed in distilled water until the equilibrium vapor pressure is achieved [4,5]. This procedure was evaluated for hydrochloric acid with determination of As, Cd, Co, Cu, Fe, Mg, Mn, Pb and Zn revealing concentrations lower than 10 ng mL^{-1} in the distillate [5]. Isothermal distillation is an inexpensive and simple technique; however, distillation rates are rather slow, since they are related to the volatility of the reagent at room temperature.

Alternatively, sub-boiling distillation uses infrared radiation, which is applied to the surface of the liquid in order to vaporize it slowly. The vaporization occurs gently, avoiding excessive boiling of the liquid and the formation of bubbles and aerosols that may suffer rupture and contaminate the distillate [6]. The vapor is condensed on a cold finger and the distillate is collected in a contamination-free container, providing a simple alternative to obtain purified acids. In addition, the choice of material and cleaning procedure of the container are extremely important for production of ultrapure acids since it may occur leaching from the vessel to the solution [7,8]. It should also be pointed out that the design of the distillation still, the temperature of the cooling water and the distance between the liquid and the heating element affect the distillation rate. Also, the analytical method chosen to analyze the ultrapure distillates is a fundamental aspect for evaluation of the quality of the distillate [2,9,10], since concentrations of contaminants are low.

The material of the distiller may also influence the quality of the distillate because there could be contamination from it and from the

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collector vessel [8,11–13]. Despite the purity of the distillate, distillation yield should also be considered an important variable and it is related to the temperature which is controlled by the power input of the apparatus [6]. A systematic study evaluating the increase of temperature up to 82 °C during the distillation procedure was performed for HNO_3 and HCl, revealing that this increment affected the production yield. When applying the highest temperature, i.e. 82 °C, the authors noticed a decrease in acidities of both acids and an increase in Al, Cu and Li concentrations for HNO_3 [14]. Regarding to the quality of the distilled acids, multiple distillation processes were also studied in order to access the quality of the distillate after successive distillation cycles of HNO_3 and HCl, but no conclusion was established about the optimal number of cycles of distillation [2,14,15]. Different variations of the sub-boiling distillation process and other methods of purifying reagents commonly used in sample preparation procedures can be found in the literature [16–18].

Nitric acid forms a type of azeotrope called maximum-boiling azeotrope; which means that the boiling temperature of the solution is higher than HNO_3 or water alone. After reaching the boiling temperature of an azeotrope, the vapor and liquid compositions are the same. Therefore, when distilling a solution of concentrated HNO_3, it is expected that the distillate contains the same acidity than the original solution [2,6,19]. However, distilling dilute HNO_3 initially produces a vapor richer in water, because the solution does not contain the same acid concentration than the azeotrope should have. Therefore, the distillate will be less acid than the original solution. When distilling HNO_3 with concentration higher than the azeotrope, there is a production of a vapor richer in HNO_3, thus condensation of this vapor allows the production of even more concentrated HNO_3 [20,21].

Previous studies have already demonstrated that HNO_3 can be separated and recovered from industrial chemical processes, thus reducing the amount of acidic waste generated [22–24]. Recently, another study evaluated the reuse of concentrated HNO_3 for successive decontamination of closed vessels after microwave-assisted digestion of sports supplements. It was found that the same acid may be reused for cleaning of vessels in combination with an additional step with ultrapure water; hence reducing HNO_3 consumption and waste generation [25]. However, none of these procedures have used sub-boiling distillation.

The possibility of recovering inorganic acids from digests ready for discard should be evaluated in order to improve green sample preparation procedures. This possibility was preliminary investigated by Nóbrega et al. [26] and by Savio et al. [27] revealing the feasibility of reusing nitric acid obtained from digests; however detailed studies were not presented. Therefore, this work aims the development of a simple and fast procedure for recovering nitric acid from sample digests using sub-boiling distillation. In this sense, the recovered acids could be reutilized, thus reducing the amount of acid waste generated.

2. Experimental

2.1. Instrumentation

Experiments were carried out using a duoPUR quartz sub-boiling system (Milestone, Sorisole, Italy) and an iCAP6000 ICP OES (Thermo Fisher Scientific, Waltham, MA, USA) operated in robust conditions and axial viewing mode. Also, Agilent 7800 Quadrupole ICP-MS (Agilent Technologies, Tokyo, JHS, Japan) was used. Argon (99.999%, White Martins-Praxair, Sertãozinho, SP, Brazil) was used for plasma maintenance, nebulization and auxiliary gas in all measurements. Plasma operating conditions and selected wavelengths and isotopes are shown in Table 1. An Ethos UP microwave oven (Milestone) was utilized for digestion of certified reference materials using the recovered nitric acid.

Table 1
Operational parameters for ICP OES and ICP-MS.

Parameter	ICP OES	ICP-MS
Radio frequency applied power (kW)	1.2	1.55
Plasma gas flow rate (L min^{-1})	12.0	15.0
Auxiliary gas flow rate (L min^{-1})	0.5	1.0
Nebulizer gas flow rate (L min^{-1})	0.50	1.00
Analyte	Emission line (λ/nm)	Isotope (*m/z*)
As	–	75
Al	–	27
Ca	317.9 (I)	44
Cd	–	111
Co	–	59
Cu	324.7 (I)	63
Fe	259.9 (I)	56
Mg	279.5 (I)	24
Mn	259.3 (I)	55
Na	588.9 (II)	23
P	213.6 (I)	31
Pb	–	208
Se	–	78
Sr	–	88
V	–	51
Zn	213.8 (I)	66

(I) Atomic emission line (II) Ionic emission line.

2.2. Reagents and standard solutions

All solutions were prepared with analytical-grade reagents and ultrapure water, with resistivity higher than 18.2 MΩ cm (Milli-Q®, Millipore, Bedford, MA, USA). Experiments were performed using HNO_3 (Synth, Diadema, Brazil, SP) purified by sub-boiling distillation. Decontamination of laboratory material was carried out by immersion in a 10% v v^{-1} HNO_3 solution during 24 h. After decontamination, all materials were washed with ultrapure water and dried in a clean laminar flow hood. Standard solutions used for ICP OES and ICP-MS calibration were prepared by appropriate dilution of 1000 mg L^{-1} stock solutions (SpecSol, Jacareí, SP, Brazil) of As, Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, P, Pb, Se, Sr, V, and Zn in 0.14 mol L^{-1} HNO_3. The concentration ranges of calibration solutions for all elements were from 0.05 to 50 µg L^{-1} for ICP-MS and from 0.05 to 40 mg L^{-1} for ICP OES measurements.

2.3. Distillation of digests from rice and bovine muscle samples

Digests of rice samples were mixed with technical grade HNO_3 (Synth) in different ratios, i.e. 1 + 1 and 1 + 4 v v^{-1}. The distillation procedure consisted in a) 2 h heating at 30% power and b) 30 min cooling step. Digests of bovine muscle were mixed with technical grade HNO_3 in ratios 1 + 1, 1 + 2, 1 + 3 and 1 + 4 v v^{-1}. A volume of 300 mL was prepared for each solution. The same distillation procedure evaluated for rice digests was applied for bovine muscle digests. Distillates were collected in pre-cleaned perfluoroalkoxy Teflon (Teflon-PFA) vessels and stored in pre-cleaned polypropylene (PP) flasks. The sub-boiling quartz apparatus was cleaned after each experiment by washing with ultrapure water, then 0.5 L of ultrapure water was distilled using the same distillation program as above, followed by distillation of concentrated HNO_3 in order to remove solid residues found in the still when solutions contained elevated concentrations of dissolved salts. Since the quartz walls of the distiller are transparent to infrared radiation, the distiller was wrapped with black cardboard and a rough estimative of temperature was made by using an infrared gun thermometer (TP-30, ThermoPro, China).

2.4. Evaluation of the recycled nitric acid

Titration with standardized NaOH solution was performed before and after each sub-boiling distillation to determine the residual acidity of the solutions. Solutions before and after sub-boiling distillation were analyzed by ICP OES and ICP-MS in order to evaluate their elemental composition. To check the quality of the recycled nitric acid, 0.5 g of NIST 1570a (Spinach Leaves) and NIST 8414 (Bovine Muscle) were digested in an Ethos UP microwave oven (Milestone) using mixtures 1 + 1 and 1 + 4 v v^{-1} obtained after sub-boiling distillation of rice digests. The heating program applied for digestion of these certified reference materials was: (i) 5 min heating until 140 °C, (ii) 5 min heating at 140 °C, (iii) 10 min heating until 180 °C, (iv) 10 min heating at 180 °C, and (iv) 30 min cooling step. Digests were diluted to 50 mL with ultrapure water and analyzed by ICP OES and ICP-MS.

3. Results and discussion

3.1. Recycling of nitric acid from rice digests

One important parameter for evaluating the digestion procedure is the residual acidity of digests. In this sense, acid-base titration was performed and residual acidities of rice digests were around 0.8 mol L^{-1}. These digests were mixed in proportions 1 + 1 and 1 + 4 v v^{-1} with technical grade HNO_3 and submitted to sub-boiling distillation. Residual acidities are shown in Table S1.

After the sub-boiling distillation procedure, 130 mL of acid were collected for the 1 + 1 v v^{-1} solution and 120 mL for the 1 + 4 v v^{-1} solution. Therefore, the experimental yield was 43% for 1 + 1 v v^{-1} and 40% for 1 + 4 v v^{-1} solutions. Despite the differences in acidities, the volumes of purified acid collected after sub-distillation were similar. Although the yields were low, the quantity of acid produced is suitable for subsequent microwave-assisted digestion procedures.

It can be seen in Table S1 that there was a decrease in acidity after the distillation for both mixtures. One possible explanation for this behavior is that when dilute nitric acid solution is distilled there is a large amount of water in the solution, thus by applying Raoult's Law principles in the distillation of a diluted azeotrope, the heating of the solution will proportionate a vapor phase containing more water than nitric acid, which reflects the dilution of the final distillate being collected in the collector vessel [20,21]. According to the phase diagram of maximum-boiling azeotrope, distilling dilute HNO_3 solutions initially produces a vapor richer in water and, if this initial distillate is not removed from the collector vessel, there will be further dilution of the acid when it is being distilled into the collector vessel. If water vapor or the initial distillate is removed from the system, there can be an increase of concentration of acid, because the vapor composition will be gradually incremented with nitric acid, until the composition of the azeotrope is achieved.

Another possibility is the loss of acid vapor caused by excessive heating of the solution, thus decomposing the nitric acid into NO_2 fumes [14]. This decomposition can be observed even below the boiling point of the azeotrope [28]. Therefore, the power input should be evaluated carefully. According to Eq. (1), the decomposition of the acid is visually observed by formation of yellowish fumes of NO_2, which indicates the thermal decomposition of nitric acid. It was observed in the final step of sub-boiling distillation the slight formation of those fumes, but this was not seemed as a major process during distillation. Estimative of temperature indicated a value of 72 ± 3 °C when applying 30% power to the sub-boiling distillation procedure. This value is close to that reported by Monticelli et al., i.e. 65 °C [14].

$$4\,HNO_3 \rightleftharpoons 4\,NO_2 + O_2 + 2\,H_2O \qquad (1)$$

The initial formation of a more dilute acid solution was observed experimentally since the first mixture (7.6 mol L^{-1} of HNO_3) produced a distillate containing 3.2 mol L^{-1} HNO_3 and the second mixture (11.3 mol L^{-1} of HNO_3) produced a distillate containing 9.1 mol L^{-1} HNO_3. Both mixtures were analyzed by ICP-MS before and after distillation to evaluate the efficiency of the decontamination and results are shown in Table 2. Sub-boiling distillation has been used to purify technical grade acids, which generally do not contain too high amounts of contaminants, with concentrations that usually fall into the µg L^{-1} range [6,12,29]. However, the developed procedure evaluated the feasibility of purifying digests containing larger amounts of contaminants, i.e. in the mg L^{-1} range or higher; thus, the efficiency of the distillation may be different from the usual procedure commonly found in the literature for purifying technical grade acids.

Table 2
Determination of As, Ca, Cu, Fe, Mg, Mn, Na, P, and Zn (µg L^{-1}) in 1 + 1 and 1 + 4 v v^{-1} solutions before and after sub-boiling distillation of rice digests by ICP-MS applying sub-boiling distillation procedure.

Element	Solution 1 + 1 v v^{-1} Before	Solution 1 + 4 v v^{-1} Before	Solution 1 + 1 v v^{-1} After	Solution 1 + 4 v v^{-1} After
As	17	5	0.3	0.1
Ca	2437	7296	1.2	1.2
Cu	410	210	1.3	0.8
Fe	620	7392	63	181
Mg	2699	1467	3.3	5.3
Mn	115	86	0.6	1.0
Na	4472	9852	315	385
P	21,914	8291	30	88
Zn	360	241	9	4
Total	33,044	34,840	423.7	666.4

If conventional distillation was applied, the vigorous boiling of the solution may result in contamination of the distillate because of two factors. There may be the formation of water films in the internal surface of the still, and these films can be carried to the condenser due to capillarity or by the vapor stream. Also, the strong boiling caused by conventional distillation generates bubbles that violently break in the surface of the liquid, throwing droplets into the vapor phase that may be carried into the condenser, thus contaminating the distillate [11].

However, in sub-boiling distillation, the gentle surface evaporation was able to remove 98.7 and 98.1% of contaminants from 1 + 1 and 1 + 4 v v^{-1} solutions, respectively. There was an appreciable removal of Ca, Mg, Na and P, which reflects the high efficiency of the sub-boiling distillation. The production of distillates with low concentrations of As, Ca, Cu, Mg, Mn and Zn was possible. However, Fe, Na and P were detected at relatively higher concentrations in the distillate. The efficiency of the distillation was different for Fe, Na and P although the initial concentrations of these elements were in the same order than Ca and Mg. It seems that there is no correlation between the initial quality of the solution and the final quality of the distillate, since Ca, Mg, Na an P were major constituents of the mixtures and the distillation efficiency was different for these elements. This observation correlates to comments of Moody and Beary that the better quality of the initial reagent will not alone guarantee the production of exceptional quality distillates [2].

The variables that affect the quality of the distillate are also the volatility of inorganic compounds and the purity of the collector vessel and quartz condenser [2]. Additionally, the values of Fe, Na and P found in the distillate might also be related to contamination, which plays a major aspect in production of ultrapure reagents [7]. Also, the sub-boiling quartz still should be cleaned after distillation cycles, since there might be the formation of solid residues in the still, which will be dissolved by the acid vapor, affecting the quality of the distillate [14].

3.2. Recycling of nitric acid from bovine muscle digests

Bovine muscle digests were mixed with technical grade HNO_3 in different ratios, i.e. 1 + 1, 1 + 2, 1 + 3, and 1 + 4 v v^{-1}. These solutions were submitted to the same distillation procedure of rice digests and solutions were analyzed by ICP-MS. Table S2 presents the results of acid-base titration and determination of As, Al, Ca, Cd, Co, Cu,

Table 3
Determination of As, Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, P, Pb, Se, Sr, V, and Zn (μg L^{-1}) in 1 + 1, 1 + 2, 1 + 3 and 1 + 4 v v^{-1} solutions before and after sub-boiling distillation procedure of bovine muscle digests.

Element	Solution 1 + 1 v v^{-1} Before	Solution 1 + 2 v v^{-1} Before	Solution 1 + 3 v v^{-1} Before	Solution 1 + 4 v v^{-1} Before	Solution 1 + 1 v v^{-1} After	Solution 1 + 2 v v^{-1} After	Solution 1 + 3 v v^{-1} After	Solution 1 + 4 v v^{-1} After
As	1.0	1.0	2.0	< 0.02	1.0	< 0.02	1.0	1.0
Al	6310	8570	5350	8270	205	83	< 4.5	< 4.5
Ca	45	< 2.04	< 2.04	< 2.04	< 2.04	< 2.04	< 2.04	< 2.04
Cd	0.6	0.6	1.1	0.4	0.4	0.9	0.5	1.0
Co	0.3	0.1	1.27	2.19	0.8	0.5	1.0	0.5
Cu	24	18	574	12	0.8	< 0.06	1.1	< 0.06
Fe	507	383	2124	531	< 0.1	< 0.1	< 0.1	< 0.1
Mg	5600	3970	5350	8270	< 1.6	< 1.6	< 1.6	< 1.6
Mn	9	10	2960	11	1.1	1.1	2.0	1.4
Na	15,430	10,740	6740	5350	< 0.2	< 0.2	< 0.2	< 0.2
P	4861	3348	10,151	1759	< 4.4	47	66	83
Pb	7.9	3.9	20.1	2.4	0.9	0.5	1.2	0.6
Se	< 0.62	< 0.62	< 0.62	< 0.62	< 0.62	< 0.62	< 0.62	< 0.62
Sr	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
V	2.0	2.5	2.4	2.3	0.7	0.4	0.8	0.4
Zn	730	490	6200	254	< 0.22	< 0.22	< 0.22	< 0.22
Total	33,528	27,537	39,476	24,464	212	133	74	87

Table 4
Determination of As, Ca, Cu, Fe, Mg, Mn, Na, P, and Zn (mg kg^{-1}, mean ± standard deviation, n = 3) and analyte recoveries calculated for NIST 8414 (Bovine Muscle) and NIST 1570a (Spinach Leaves).

Element	Certified value (mg kg^{-1})		Determined value (mg kg^{-1})				Recovery (%)			
	NIST 8414	NIST 1570a	NIST 8414 1 + 1 v v^{-1}	NIST 8414 1 + 4 v v^{-1}	NIST 1570a 1 + 1 v v^{-1}	NIST 1570a 1 + 4 v v^{-1}	NIST 8414 1 + 1	NIST 8414 1 + 4	NIST 1570a 1 + 1	NIST 1570a 1 + 4
As	0.009 ± 0.003	0.07 ± 0.01	0.010 ± 0.003	0.0076 ± 0.0003	0.067 ± 0.003	0.100 ± 0.004	106 ± 3	84 ± 4	100 ± 4	96 ± 4
Ca	145 ± 20	1.53 ± 0.04 [a]	148.5 ± 0.3	143 ± 18	1.30 ± 0.04 [a]	1.25 ± 0.03 [a]	102.4 ± 0.2	99 ± 2	85 ± 3	82 ± 2
Cu	2.8 ± 0.45	12.2 ± 0.6	2.38 ± 0.06	2.6 ± 0.2	12.1 ± 0.8	11.7 ± 0.5	85 ± 2	92 ± 8	99 ± 6	96 ± 4
Fe	71 ± 9	–	60 ± 2	67 ± 6	–	–	84 ± 3	94 ± 9	–	–
Mg	960 ± 95	0.89 * [a]	951.7 ± 0.5	982 ± 69	0.84 ± 0.03	0.81 ± 0.02	99.1 ± 0.1	102 ± 7	94 ± 3	91 ± 2
Mn	0.37 ± 0.09	76 ± 2	0.32 ± 0.02	0.39 ± 0.04	63 ± 4	61 ± 2	87 ± 7	106 ± 8	83 ± 5	80 ± 3
Na	2100 ± 100	1.82 ± 0.04 [a]	2057 ± 15	2078 ± 227	1.65 ± 0.05	1.60 ± 0.04	98.0 ± 0.7	99 ± 8	91 ± 2	88 ± 2
P	8360 ± 450	0.52 ± 0.01 [a]	7510 ± 185	6938 ± 540	0.50 ± 0.02 [a]	0.44 ± 0.02 [a]	90 ± 2	83 ± 5	96 ± 4	86 ± 3
Zn	142 ± 14	82 ± 3	117 ± 22	108 ± 8	67 ± 2	60 ± 2	83 ± 2	76 ± 5	82 ± 3	73 ± 3

(*) Non-certified value (a) Value in % w w^{-1} (-) Value not informed

Fe, Mg, Mn, Na, P, Pb, Se, Sr, V, and Zn is shown in Table 3.

All solutions presented a decrease in acidities after sub-boiling distillation. However, even the acid produced after distillation of 1 + 1 v v^{-1} solution is suitable for microwave-assisted digestion, since studies have demonstrated the applicability of dilute HNO_3 for digestion of different organic matrices [30–33].

The efficiencies in removing contaminants were 99.4, 99.5, 99.8 and 99.6% for 1 + 1, 1 + 2, 1 + 3, and 1 + 4 v v^{-1} solutions, respectively. Collected volumes of purified acids were around 120–140 mL for all solutions. Sub-boiling distillation was effective for removing significant quantities of contaminants, such as Al, Mg, Na, P, and Zn. Solutions 1 + 1 and 1 + 2 v v^{-1} contained concentrations of Al of 205 and 83 μg L^{-1}, respectively, which corresponds to 97 and 63% of the total amounts of residual contaminants. Solutions 1 + 3 and 1 + 4 v v^{-1} were affected by the presence of P in the distillates, which corresponds to 89 and 95% of total values, respectively. Also, the presence of contaminants was observed after sub-boiling distillation of hydrochloric and nitric acids in another study [14]. Some authors reported different contaminant levels for Al, Ca, Cu, Fe, Mg, Ni, Pb and Zn when preparing sub-boiled distilled inorganic acids in chemical laboratories or in clean rooms; hence, as expected, the environment in which the distillation is carried out also implies in possible contamination issues of distillates [28].

The concentrations of contaminants in 1 + 1, 1 + 2, 1 + 3 and 1 + 4 v v^{-1} solutions were in the same order than 1 + 1 and 1 + 4 v v^{-1} solutions of rice digests shown in Table 2. Both procedures produced distillates with high purity, with efficiencies higher than 99% for both of them; however, contamination of Fe, Na and P occurred in distillates of rice digests. These elements were below the limits of detection of the method in bovine muscle distillates obtained after distillation of bovine muscle digests, which reinforces the hypothesis of contamination of distillates obtained in Table 2. However, it seems that P was present in all distillates, with exception of the one produced after distillation of 1 + 1 v v^{-1} solution, this behavior might be related to contamination. It was noticed that after the distillation of residues, there was a remaining deposit of solids in the quartz walls, which may have caused contamination by leaching of elements into the vapor phase. Thus, it might also have caused the contamination of Cd and Co in 1 + 1 and 1 + 2 v v^{-1} solutions because initial concentrations were lower than the values obtained after distillation. If this contamination issue is effectively related to the distillation process, it may be solved by applying a further cleaning step after acid production.

3.3. *Investigation of the reuse of nitric acid*

It is important to mention that some contaminants found in the distillates may influence recoveries when the acid is used for performing further digestions. In this sense, Table 4 presents certified values for spinach leaves and bovine muscle digests and recoveries calculated for As, Ca, Cu, Fe, Mg, Mn, Na, P, and Zn. To check if the contaminants that remained in the acid influenced recoveries, a careful review of concentrations shown in Table 3 for 1 + 1 and 1 + 4 v v^{-1}

solutions should be done.

Acceptable recoveries were found for As, Ca, Cu, Fe, Mg, Mn, Na, and P, thus demonstrating that sub-boiled nitric acid is suitable for microwave-assisted digestion of animal and plant tissues. Recoveries below 80% were only found for Zn in both samples when using 1 + 4 v v^{-1} solution. By comparison, results were similar for most determined elements, with exception of Zn in 1 + 4 v v^{-1} solution. Thus, the ratio of volume of sample digest and volume of technical grade HNO_3 did not seem to influence significantly the calculated recoveries for spinach leaves and bovine muscles certified reference materials.

4. Conclusions

A procedure for recover and reuse of nitric acid from sample digests was developed and its feasibility was demonstrated. As discussed, all evaluated mixtures had their acidity decreased due to aspects related to the Raoult's Law and the distillation of azeotropes. All recovered acids contained acidities between 3.1 and 9.2 mol L^{-1}, which are suitable for further reuse in microwave-assisted digestions. Despite some unexpected residual contaminants, it seems that the ratio of digest and technical grade acid did not affect the quality of the distillates. Also, the efficiency in contaminant removal was calculated taking into account the initial and final concentration of contaminants, and ranged from 98.1 to 99.8% for all evaluated sub-boiling distillation procedures.

Although slight degree of contamination was observed for Al, Fe, Na, and P in some distillates, recoveries obtained for digestions of certified reference materials varied from 73 to 106%. There was no significant difference in recoveries when different mixtures containing nitric acid digests plus technical grade nitric acid were evaluated, so, in order to follow green chemistry recommendations, i.e. reduce, recycle, and reuse, the application of the sub-boiling distillation purification procedure for 1 + 1 v v^{-1} solution is recommended, because it consumes a larger amount of sample digest residues and lower amounts of technical grade reagents. It is important to observe that in all cases the acidity and volume of the recycled acids are suitable for subsequent reuse. Therefore, there is a reduction in the volume of residues generated after microwave-assisted digestion procedures and nitric acid from sample digests can be recovered and reused.

CRediT authorship contribution statement

Matheus L. de Mello: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Lucimar L. Fialho:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Camillo Pirola:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing. **Joaquim A. Nóbrega:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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