



## A review of reflux systems using cold finger for sample preparation in the determination of volatile elements

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### ABSTRACT

The present paper presents advantages, limitations and applications of a reflux system (cold finger) employed for sample preparation during determination of volatile elements. Also other techniques employed for sample preparation in the determination of volatile elements are discussed and compared. A list of ten papers published reporting use of cold finger as reflux system are being cited and discussed.

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### 1. Introduction

Arsenic, antimony, cadmium, lead and mercury are chemical elements of great toxicity, which are often determined in environmental, geological, food and biological samples [1–3]. The quantification of these elements is relatively easy, considering mainly the spectrometric methods available [4–6]. However, the sample preparation step is almost always complicated due to the volatile character of these elements [7].

The wet-ashing method is the technique more used for sample preparation in inorganic analysis [8,9]. This is carried out with addition of an acid or mixtures of acids, in open vessels or in tubes, on hot plates or in aluminum blocks with thermal heating. This technique can be used for mineralization of all types of samples. Furthermore, the sample masses and the acid volumes used in the procedures are not critically restricted. Despite these advantages, this technique cannot be used for sample digestion for determination of volatile species.

Nowadays, the microwave-assisted digestion with pressurized closed-vessel systems is the technique most widely used for sample preparation during determination of volatile species [10–12]. Microwave heating has several advantages over conventional heating: the digestion time is shorter; the amount of reagent required for mineralization is reduced; the risk of sample contamination is also reduced. However, the main limitation is the time required for cooling the

vessel, which may take hours. The open focused microwave-assisted equipment operates under atmospheric pressure. These systems are safe, versatile; and allow control of microwave energy released to the sample. However, loss of volatile elements cannot be excluded in open-vessel digestion [13].

Procedures involving Parr digestion bombs were widely used in the past for sample mineralization during determination of volatile species. These are closed systems that are heated by convection using conventional oven. In these procedures, the sample amount used for digestion is rigorously controlled because of risk of explosions [14–16].

The microwave acid digestion bombs are pressurized systems, which were developed with plastic material allowing heating with microwave radiation, using conventional oven [17,18]. These provide: fast digestion times, temperatures to 250 °C, pressures to 1200 psi and complete containment of volatiles. Also the mass and nature of the sample are critical parameters due to the risk of explosions. Recently, these bombs were employed for sample digestion of chicken samples for determination of arsenic [19].

Procedures based on the formation of magnesium compounds have been also proposed for sample preparation in the determination of volatile elements. First, the sample in the presence of magnesium nitrate, magnesium oxide and nitric acid is evaporated to dryness in sand bath. Afterward, the residue is calcined in muffle furnace up to 450 °C with gradual increase in temperature. The white ashes are dissolved with hydrochloric acid solution. The analysis of several certified reference materials has confirmed the efficiency this digestion procedure. The main disadvantage is the risk of contamination due to large amount of magnesium reagents that are used. This strategy has been employed

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during determination of arsenic [20], antimony [21], tellurium [22], and selenium [23].

Slurry sampling is another strategy widely used in recent times for sample preparation during determination of volatile elements employing spectrometric methods [24]. This technique involves handling of sample with diluted acid solutions, reducing the risk of contamination by reagents, under room temperature or eventually under temperature conditions that are not critical to loss of volatile elements. Sample masses and reagent volumes are not critical parameters, such as occur in microwave-assisted digestion with pressurized closed-vessel methods. Slurry sampling allows also the development of procedures of sample preparation for speciation analysis methods involving volatile species as mercury [25], arsenic [26–28] and antimony [29,30]. Obviously, this would not be possible using microwave-assisted digestion or wet-ashing.

Solid sampling [31] constitutes today the most promising technique for determination of volatile species. The elements can be determined without use of reagents, without heating step, and higher sensitivity than the slurry sampling because of the avoidance of analyte dilution. Another distinct advantage of direct solid sampling is that samples of different textures can be readily analyzed without further hindrance.

The sample preparation technique involving “cold finger system” allows procedures of sample digestion for determination of volatile elements. The loss by volatilization is avoided due to the condensation of the volatile species, under the reflux system formed by the cold finger. This technique combines the advantages of the wet-ashing technique, which are: sample masses and reagent volumes are not critical parameters for the experiments; the risk of explosion is minimal; and application for mineralization of several types of samples, including organic and inorganic matrices.

## 2. Sample preparation involving acid digestion with heating under reflux

### 2.1. Use of reflux condenser for condensation of volatile chemical elements

The first sample preparation methods involving reflux system for condensation of volatile chemical elements were established using conventional condensers. These are highly effective for condensation of the volatile species but are not practical when the number of samples for digestion is large.

Nieuwenhuize et al. used reflux condenser in sample preparation procedure for digestion of soil, sediment and sludge during determination of cadmium, chromium, copper, iron, manganese, lead and zinc employing flame absorption spectrometry. The results obtained were compared with those found using a microwave-assisted digestion procedure. Statistical test demonstrated that there is no significant difference between the analytical results achieved by two methods [32].

Saraswati and co-workers proposed wet digestion procedures employing reflux condenser and mixture formed by nitric acid, sulfuric acid and perchloric acid for determination of arsenic and selenium by HG AAS and mercury using CV AAS in certified reference materials of spinach and tomato leaves [33], estuarine sediment [34] and sludge [35].

Ducros et al. proposed a method for the determination of selenium in biological samples employing microwave digestion in an open-vessel system by heating under reflux with nitric acid and hydrogen peroxide. This method is fast and without the use of perchloric acid [36].

### 2.2. Use of cold finger as reflux system in sample preparation

#### 2.2.1. Fundamental principles of cold finger

The “cold finger” is a glass tube in the shape of finger that is placed over the digester tube during procedures of acid digestion with heating. In the cold finger tube water is put in order to cool the superior part of the tube digester, thus causing reflux and condensation of volatile species,

avoiding the loss by evaporation. In these processes, the acids used for digestion are also condensed by reflux.

The return of the acid for the digestion flask due to condensation is regarded as an advantage and also a disadvantage. The advantage is that during the digestion process generally addition of reagents is not required, as almost always occurs in conventional procedures with open system. Consequently, fewer reagents are consumed and thus the risk of contamination by these will be lower. This justifies the use of this reflux system in sample digestion procedures for the determination of non-volatile elements such as calcium, magnesium, manganese, copper and etc. [37].

The disadvantage is that residual solutions of the digestion processes developed using the system reflux usually have a high acid concentration. This inconvenience, when possible has been solved by diluting the final solution obtained in the digestion process. Another option is to prepare the solutions of the calibration curves with the acid concentration close to the acid concentration of the samples digested, avoiding thus the matrix effect.

In our laboratory, these digestion processes have been performed in digester block of aluminum with capacity for 40 runs and, digester flask and cold finger tube with volumes of 90 and 40 mL, respectively. During a digestion process the amount of refrigeration water put in the tube is from 34 to 36 mL.

The schematic diagram of the digestion system is shown in Fig. 1. In it can be seen the cold finger (a), digester tube (b) and cold finger coupled to digester tube (c).

#### 2.2.2. Applications of cold finger system in sample preparation procedures

Several authors have used this system in sample digestion process [38–47].

Nano et al. established a sample digestion procedure using cold finger for the determination of the elements: arsenic, cadmium, barium, calcium, copper, iron, magnesium, manganese and zinc in oyster tissue using inductively coupled plasma optical emission spectrometry. The proportion of the reagents: hydrochloric acid, nitric acid and peroxide hydrogen was optimized employing a simplex centroid statistical mixture design, being that all experiments were performed using a standard reference material of oyster tissue. The procedure proposed recommends a mixture with composition of 21.4% for hydrochloric acid, 30.8% for nitric acid and 47.8% for peroxide hydrogen, considering commercial solutions. The validation studies evidenced a good efficiency of digestion procedure with recoveries between 84% and 110% [38].

Ferreira et al. proposed a direct method for the determination of cadmium in wines by ET AAS. During the validation process another method was also developed involving complete digestion with concentrated nitric acid and hydrogen peroxide under reflux (cold finger system) for 2 h. The linear regression method was used to compare the analytical results obtained with these two methods. The results demonstrated that there is no evidence for a systematic difference between the two methods for the determination of cadmium in wine [39].

Macedo et al. proposed a method for the determination of total arsenic in phosphate fertilizers and phosphate rocks by HG AAS. The digestion procedure was performed using concentrated nitric acid and hydrogen peroxide under reflux for 4 h employing cold finger. The analysis of the certified reference material of marine sediment demonstrated the accuracy of this procedure. The samples were also analyzed by another method employing slurry sampling and HG AAS. A statistical test proved that there is no significant difference between the analytical results achieved by these two methods [40].

Another paper used cold finger in sample preparation step of an analytical procedure for the determination of total arsenic in airborne particulate matter by HG AAS. The digestion was made using concentrated nitric acid under reflux for 2 h. The accuracy was confirmed by analysis of a certified reference material of particulate matter [41].

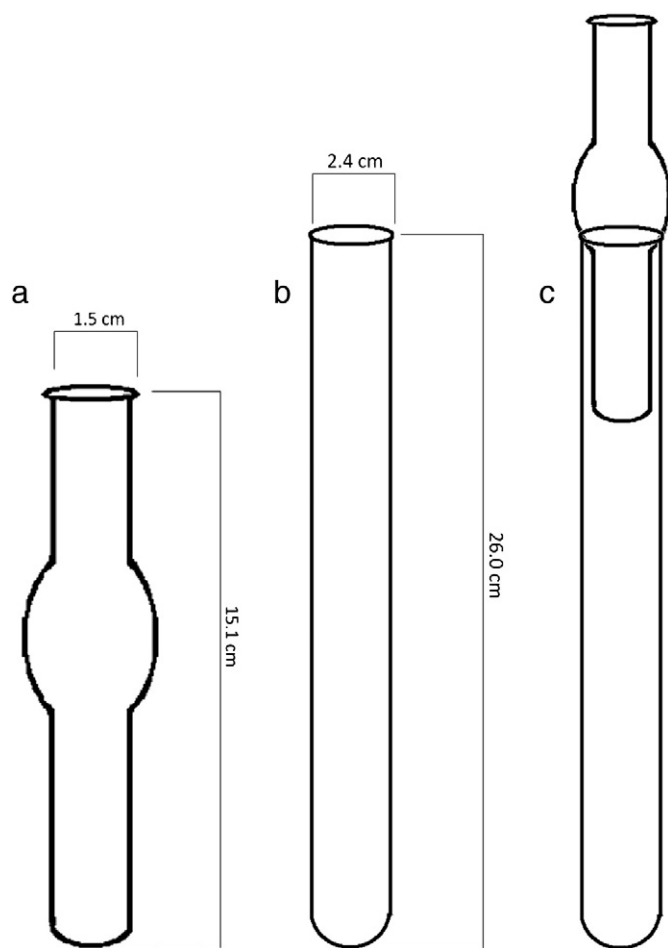


Fig. 1. Schematic diagram. a. Cold finger tube; b. Digestion tube; c. Cold finger tube coupled to digestion tube.

A complete study evaluated the performance of a digestion procedure under reflux using cold finger for the determination of lead in plant foods employing ET AAS. The samples were digested for 4 h using concentrated nitric acid and hydrogen peroxide. In this paper, considering that during the digestion step the concentrated nitric acid used is not volatilized, the external calibration technique employing aqueous standards was established with efficiency for  $2.6 \text{ mol L}^{-1}$  nitric acid solutions. It was observed that the acid concentrations of the residual solution after digestion varied from 2.4 to  $2.8 \text{ mol L}^{-1}$ . The accuracy of the method was confirmed by analysis of two certified reference materials of leaves [42].

Dessuy et al. developed a method for determination of cadmium and lead in beverages by ET AAS. The digestion procedure employed nitric acid and hydrogen peroxide and heating under reflux using cold finger [43].

Andrade et al. determined lead in sugar cane employing ICP-MS as analytical technique. The digestion process involved concentrated nitric acid with heating in digester block under reflux using cold finger system [44].

Silva et al. used concentrated nitric acid, peroxide hydrogen and a reflux system with cold finger for digestion of rice samples for the determination of cadmium employing ET AAS. The cadmium standard solutions used for the external calibration technique were prepared using 2.6 M nitric acid solutions of concentration, considering the acid content of the residual solutions from digestion process that varied of 2.4 to 2.7 M. The accuracy was confirmed by analysis of a certified reference material of rice flour [45].

Becker et al. performed a method for the determination of arsenic in gasoline by HG AAS. The sample preparation process using reflux

system with cold finger was established in two steps: firstly, the sample was digested with concentrated sulfuric acid for 4 h, and after concentrated nitric acid and peroxide hydrogen were added to conclude the digestion process. The accuracy of this digestion procedure was confirmed by analysis of the certified reference material of residual fuel oil (NIST SRM 1634c Trace Elements in Fuel Oil) [46].

Ribeiro et al. [47] proposes a "cold finger" with a new design as reflux system in procedure of decomposition of biological samples for the determination of mercury. In this work, the effect of temperature was studied in order to compare the cold finger system with the conventional wet-ashing method (open system) during the digestion of different species of mercury. Experiments were performed at temperatures of: 80, 100 and  $120 \text{ }^\circ\text{C}$ , for the species: mercury (II) ion, methyl mercury and ethyl mercury, all with final concentration of  $5.0 \text{ } \mu\text{g L}^{-1}$ , being the final mercury concentration determined by CV AAS. The results for mercury (II) ion after the digestion using conventional system demonstrated a slight decrease in the initially concentration of mercury, with the increase of the temperature, which evidences analyte losses by volatilization. However, digestion in the presence of the cold finger system provides results with constant concentration for mercury. Digestion of methyl-mercury(+) and ethyl-mercury(+) in the experimental conditions of: temperature of 80 and  $100 \text{ }^\circ\text{C}$  and digestion time of 2 h showed a low recovery for mercury for both digester systems used (open system and cold finger). However, for the temperature of  $120 \text{ }^\circ\text{C}$  and digestion time of 2 h, quantitative recoveries were found for both mercury species. The authors concluded that the use of low temperature of digestion and a relatively short time is not effective to complete the conversion of organic species of this metal to its inorganic form. Thus, the procedure established for the determination of total mercury in this kind of sample recommended a digestion step for 2 h at the temperature of  $120 \text{ }^\circ\text{C}$ , which is the boiling point temperature of nitric acid. The authors observed also that the heating of the digester tube (at temperature of  $120 \text{ }^\circ\text{C}$ ) without the use of cold finger promotes the dryness of this tube. When the cold finger system is used, this fact does not occur. This work evaluated also the efficiency of the digestion process by determination of total organic carbon and residual acidity during the mineralization of three biological samples employing the open system and the cold finger system. For total organic carbon the results were 15.4% for the open system and 20.8% using the cold finger system. The authors concluded that the cold finger system avoids the losses by volatilization of volatile organic compounds. These data were not conclusive to evaluate the efficiency of the two digestion methods. The results for residual acidity demonstrated a reduction of 18% for the open system in comparison with the cold finger system. These results also confirmed that the acid is not lost during digestion using the cold finger.

### 3. Conclusions

Most of the published papers involving reflux system using cold finger were developed as alternative methods to evaluate the accuracy of other methods. Thus, the information about the performance of this system in these papers is very limited. Only three papers were performed using the cold finger system as main subject of the work.

During a sample digestion process using reflux by cold finger, the acid that is not consumed by the sample is not eliminated by evaporation. Thus, the residual acidity should be measured, for that the standard solutions used for external calibration should have the same acid concentration.

Considering that the acid used for digestion is not lost by volatilization. The amounts required are lower, reducing the risk of contamination due to reagent addition.

The conventional condensers with continuous water flow are efficient for condensation of the volatile species; however the experimental work is complicated when the sample number is large.

The bibliographic revision reports that cadmium, lead, arsenic, antimony and mercury have been determined in several samples after

acid digestion with heating under reflux using cold finger. It was not found papers involving selenium and tellurium.

Acid digestion using reflux system with cold finger is a simple and economic strategy, which can be applied for mineralization of several types of samples. The main disadvantage of this technique is the time taken for digestion which is relatively high compared with other procedures.

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### References

- [1] J. Mutic, D. Manojlovic, R. Kovacevic, J. Trifunovic, N.R. Amaizah, L. Ignjatovic, *Microchem. J.* 98 (2011) 11–14.
- [2] C. Garcia-Sartal, V. Romaris-Hortas, M. del Carmen Barciela-Alonso, A. Moreda-Pineiro, R. Dominguez-Gonzalez, P. Bermejo-Barrera, *Microchem. J.* 98 (2011) 91–96.
- [3] Z. Fu, F. Wu, C. Mo, B. Liu, J. Zhu, Q. Deng, H. Liao, Y. Zhang, *Microchem. J.* 97 (2011) 12–19.
- [4] Z. Long, Y. Luo, C.B. Zheng, P.C. Deng, X.D. Hou, *Appl. Spectrosc. Rev.* 47 (2012) 382–413.
- [5] H. Matusiewicz, R.E. Sturgeon, *Appl. Spectrosc. Rev.* 47 (2012) 41–82.
- [6] M. Welna, W. Zyrnicki, *Anal. Lett.* 44 (2011) 942–953.
- [7] M.A.Z. Arruda, *Trends in sample preparation*, Nova Science Publishers, New York, 2007.
- [8] M.D.A. Korn, E.S.D. Morte, D.C.M.B. dos Santos, J.T. Castro, J.T.P. Barbosa, A.P. Teixeira, A.P. Fernandes, B. Welz, W.P.C. dos Santos, E.B.G.N. dos Santos, M. Korn, *Appl. Spectrosc. Rev.* 43 (2008) 67–92.
- [9] P. Pohl, H. Stecka, I. Sergiel, P. Jamroz, *Food Anal. Methods* 5 (2012) 737–751.
- [10] M.J. da Silva, A.P.S. Paim, M.F. Pimentel, M.L. Cervera, M. de la Guardia, *Anal. Chim. Acta* 667 (2010) 43–48.
- [11] G. Grindlay, J. Mora, L. Gras, M.T.C. de Loos-Vollebregt, *Anal. Chim. Acta* 691 (2011) 18–32.
- [12] C.A. Bizzi, E.M.M. Flores, J.S. Barin, E.E. Garcia, J.A. Nobrega, *Microchem. J.* 99 (2011) 193–196.
- [13] L.M. Costa, D.C.M.B. Santos, V. Hatje, J.A. Nobrega, M.G.A. Korn, *J. Food Compos. Anal.* 22 (2009) 238–241.
- [14] J.E. Tahan, V.A. Granadillo, J.M. Sanchez, H.S. Cubillan, R.A. Romero, *J. Anal. At. Spectrom.* 8 (1993) 1005–1010.
- [15] S.C. Foo, T.C. Tan, *Sci. Total. Environ.* 209 (1998) 185–192.
- [16] A.A. Karanasiou, N.S. Thomaidis, K. Eleftheriadis, P.A. Siskos, *Talanta* 65 (2005) 1196–1202.
- [17] B. Bernas, *Anal. Chem.* 40 (1968) 1682–1686.
- [18] D.R. Vieira, J.T. Castro, V.A. Lemos, *J. AOAC Int.* 94 (2011) 645–649.
- [19] A.S. dos Passos, T.S. Neri, M.V. Maciel, I.L. Romao, V.A. Lemos, *Food Addit. Contam.*, In press, <http://dx.doi.org/10.1080/19440049.2012.706833>.
- [20] P. Cava-Montesinos, M.L. Cervera, A. Pastor, M. de la Guardia, *Talanta* 60 (2003) 787–799.
- [21] M.N.M. Reyes, M.L. Cervera, M. de la Guardia, *J. Braz. Chem. Soc.* 22 (2011) 197–203.
- [22] P. Cava-Montesinos, M.L. Cervera, A. Pastor, M. de la Guardia, *Anal. Chim. Acta* 481 (2003) 291–300.
- [23] M.N. Matos-Reyes, M.L. Cervera, R.C. Campos, M. De La Guardia, *Food Chem.* 122 (2010) 188–194.
- [24] S.L.C. Ferreira, M. Miro, E.G.P. da Silva, G.D. Matos, P.S. dos Reis, G.C. Brandao, W.N.L. dos Santos, A.T. Duarte, M.G.R. Vale, R.G.O. Araujo, *Appl. Spectrosc. Rev.* 45 (2010) 44–62.
- [25] S.R. Segade, J.F. Tyson, *Talanta* 71 (2007) 1696–1702.
- [26] P. Cava-Montesinos, P.A. de la Guardia, C. Teutsch, M.L. Cervera, M. de la Guardia, *Anal. Chim. Acta* 493 (2003) 195–203.
- [27] S.M. Macedo, R.M. de Jesus, K.S. Garcia, V. Hatje, A.F.S. Queiroz, S.L.C. Ferreira, *Talanta* 80 (2009) 974–979.
- [28] V. Hatje, S.M. Macedo, R.M. de Jesus, G. Cotrim, K.S. Garcia, A.F. de Queiroz, S.L.C. Ferreira, *Mar. Pollut. Bull.* 60 (2010) 2225–2232.
- [29] S.L.C. Ferreira, S.M. Macedo, D.C. dos Santos, R.M. de Jesus, W.N.L. dos Santos, A.F.S. Queiroz, J.B. de Andrade, *J. Anal. At. Spectrom.* 26 (2011) 1887–1891.
- [30] A. Ilander, A. Vaisanen, *Anal. Chim. Acta* 689 (2011) 178–183.
- [31] B. Welz, M.G.R. Vale, D.L.G. Borges, U. Heitmann, *Anal. Bioanal. Chem.* 389 (2007) 2085–2095.
- [32] J. Nieuwenhuize, C.H. Poley-Vos, A.H. van den Akker, W. van Delft, *Analyst* 116 (1991) 347–351.
- [33] R. Saraswati, R.L. Watters, *Talanta* 41 (1994) 1785–1790.
- [34] R. Saraswati, T.W. Vetter, R.L. Watters, *Microchim. Acta* 118 (1995) 163–175.
- [35] R. Saraswati, T.W. Vetter, R.L. Watters, *Analyst* 120 (1995) 95–99.
- [36] V. Ducros, D. Ruffieux, N. Belin, A. Favier, *Analyst* 119 (1994) 1715–1717.
- [37] A.V. Zmozinski, A. de Jesus, M.G.R. Vale, M.M. Silva, *Talanta* 83 (2010) 637–643.
- [38] R.M.W. Nano, R.E. Bruns, S.L.C. Ferreira, N. Baccan, S. Cadore, *Talanta* 80 (2009) 559–564.
- [39] S.L.C. Ferreira, R.M. de Jesus, G.D. Matos, J.B. de Andrade, R.E. Bruns, W.N.L. dos Santos, D.D. Cavalcante, M.G.R. Vale, M.B. Dessuy, *J. Braz. Chem. Soc.* 20 (2009) 788–794.
- [40] S.M. Macedo, R.M. de Jesus, K.S. Garcia, V. Hatje, A.F.D. Queiroz, S.L.C. Ferreira, *Talanta* 80 (2009) 974–979.
- [41] S.M. Macedo, D.C. dos Santos, R.M. de Jesus, G.O. da Rocha, S.L.C. Ferreira, J.B. de Andrade, *Microchem. J.* 96 (2010) 46–49.
- [42] R.M. de Jesus, M.M.S. Junior, G.D. Matos, A.M.P. dos Santos, S.L.C. Ferreira, *J. AOAC Int.* 94 (2011) 942–946.
- [43] M.B. Dessuy, M.G.R. Valea, B. Welz, A.R. Borgesa, M.M. Silva, P.B. Martelli, *Talanta* 85 (2011) 681–686.
- [44] S.L.C. Ferreira, L.A. Portugal, G.D. Matos, D.G. da Silva, R.M. de Jesus, G.B. Brito, *Anal. Methods* 3 (2011) 1168–1171.
- [45] D.G. da Silva, M.M.S. Junior, L.O.B. Silva, L.A. Portugal, G.D. Matos, S.L.C. Ferreira, *Anal. Methods* 3 (2011) 2495–2500.
- [46] E.M. Becker, M.B. Dessuy, W. Boschetti, M.G.R. Vale, S.L.C. Ferreira, B. Welz, *Spectrochim. Acta B* 71–72 (2012) 102–106.
- [47] E.Q. Oreste, A. de Jesus, R.M. de Oliveira, M.M. da Silva, M.A. Vieira, A.S. Ribeiro, *Microchem. J.* (2012), In press, <http://dx.doi.org/10.1016/j.microc.2012.05.034>.