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Article

Infra-red Heating as an Alternative Technique for Fast Sample Preparation

Sandro T. Gouveia[a]***, Orlando Fatibello-Filho***[b] ***and Joaquim A. Nóbrega***[b*]

[a]*Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Fortaleza - CE, Brazil*
[b]*Departamento de Química, Universidade Federal de São Carlos, CP 676, 13560-970, São Carlos - SP, Brazil*

Neste trabalho investigou-se um procedimento de preparo de amostras, com rápido aquecimento da suspensão da amostra em meio ácido usando radiação infravermelho emitida por lâmpadas de tungstênio. As vantagens do procedimento proposto são a simplicidade e o baixo custo. A solução diluída do ácido é aquecida em tempo inferior a 60 s e o tempo total do preparo da amostra é menor que 5 min. O procedimento proposto pode ser facilmente implementado para a análise de elementos presentes em baixas concentrações. Avaliações preliminares foram feitas determinando-se os teores de Cu, Fe, Mn e Zn em material de referência certificado de fígado bovino e folha de maçã. Todos os resultados foram avaliados com nível de confiança de 95%. Os teores determinados de Cu e Mn foram comparados em amostra de fígado bovino sem tratamento prévio ou após liofilização. Para essa amostra, os resultados foram validados empregando-se procedimento de decomposição assistida por microondas em frasco fechado.

A procedure for sample preparation was investigated in this work using infra-red radiation generated by tungsten lamps for fast heating of an acidic sample suspension contained in a glass flask. The main advantages of the developed procedure are its simplicity and low-cost. Additionally the dilute acid solution is heated in less than 60 s and the total sample preparation is performed in less than 5 min. The proposed procedure is suitable for trace analysis and it can be easily implemented. The preliminary investigations focus on the determination of Cu, Fe, Mn, and Zn in bovine liver and apple leaves as standard reference materials. All results are in agreement at a 95% confidence level. Copper and Mn were also determined in a sample of bovine liver without any sample pretreatment or after a freeze-drying step for comparison. For this sample, the results were validated using a conventional microwave-assisted closed vessel procedure.

Keywords: Infra-red heating; sample preparation; infra-red radiation; sample decomposition

Introduction

The analytical sciences have rapidly evolved with respect to the development of modern techniques for measuring inorganic and organic analytes in liquid medium. The sample preparation step still needs improvement and this is most critical for samples that contain a chemically resistant matrix, either organic or inorganic, with analytes present in low concentrations.

The use of microwave radiation as a heating source is well-established in analytical chemistry and a plethora of procedures were established based on microwave-assisted digestion[1]. There is no doubt that these procedures are useful and that they paved a new method for sample preparation. Modern instrumentation allows improvement of the performance of microwave-assisted procedures by measuring and controlling the temperature and the pressure and therefore improving safety.

The employment of other radiations, such as ultraviolet[2] and ultrasound[3,4], has also been proposed for sample preparation purposes. Ultraviolet radiation is well-established for decomposition of organic compounds in enviromental samples[5].

Infra-red radiation could be more extensively used based on its ability to promote fast heating of solutions. Infra-red radiation is usually employed for drying samples in cleaner conditions and for the preparation of sub-boiling acids[6]. Another interesting application of infra-red is the heating of liquid or solid samples for determination of volatile analytes[7]. This procedure was successfully applied for determination of iodine in milk samples[8].

Some less conventional applications of infra-red radiation in analytical chemistry were proposed by Campos *et al.*[9] and

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[*] e-mail: djan@zaz.com.br

by Magalhães *et al.*[10]. Both groups used an arrangement with three tungsten lamps for direct analysis of solid samples. The former authors employed this system to burn organic samples and the volatile elements were transported by a gas flow carrier towards a flame AAS[9]. In the other investigation this device was used to volatilize Hg from sediment samples[10].

In this work three 150 W tungsten lamps configured in a triangular arrangement were employed to heat a glass flask containing the sample. The proposed procedure was evaluated for determination of Cu, Fe, Mn and Zn in a botanical and in a biological sample.

Experimental

Reagents, samples and apparatus

All reagents were analytical reagent grade and all solutions were prepared using Milli-Q water (Millipore, 18 mΩ cm^{-1}, USA). Hydrogen peroxide and HNO_3 concentrated (Mallinckrodt, Germany) were used as received. Diluted solutions of Cu, Fe, Mn, and Zn were prepared from monoelement stock solutions containing 1,000 mg l^{-1} of each metals (Merck, Germany). The decomposition was carried out in a 20 ml borosilicate glass flask with a PTFE cap.

Several standard reference materials (SRM) from the National Institute of Standards and Technology (NIST) were employed during this investigation. Most experiments dealt with one biological reference material (bovine liver, SRM 1577b, NIST, USA) and one botanical reference material (apple leaves, SRM 1515, NIST, USA). Four bovine liver samples were employed as received to evaluate the performance of the procedure. For validating the results obtained with the proposed procedure, these samples were also acid decomposed employing a microwave-assisted closed vessel (Milestone, ETHOS 1600, Germany).

In all digested solutions the determination of Cu and Mn was carried out by graphite furnace atomic absorption spectrophotometry (GFAAS, SpectrAA 800, Varian, Australia) with a Zeeman background corrector. Iron and Zn were determined in the SRM's by flame atomic absorption spectrophotometry (FAAS, SpectrAA 640, Varian, Australia).

A schematic diagram of the infra-red heating system is shown in Figure 1. Three 15 V-150 W infra-red lamps (Osram, Halogen-Bellaphort, Germany) were electrically connected in series. The lamps were set in a triangular arrangement to form a common focal point for all the lamps. They were connected to a Variac transformer (SP Sociedade Técnica Paulista LTDA, Brazil).

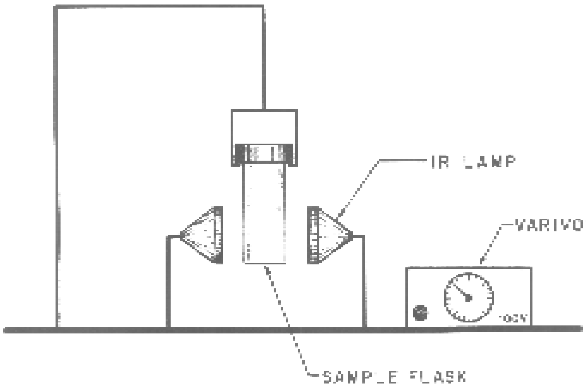

Figure 1. Infra-red decomposition arrangement. The third lamp (not shown) is positioned behind the sample flask.

Procedure

Bovine liver samples with masses varying from 200 to 1400 mg were employed for evaluating the effect of sample masses on the decomposition using the tungsten lamp system. The decomposition was evaluated using 1.0 ml of HNO_3 conc. plus H_2O_2 conc. solution with volumes varying from 0 to 1.0 ml in 0.5 ml aliquots. Afterwards, the volume of the H_2O_2 conc. solution was fixed in 1.0 ml and the volume of the HNO_3 conc. solution varied from 0.5 to 1.5 ml in 0.5 ml aliquots. For validation of the obtained results for Cu and Mn, these samples were also decomposed using a microwave-assisted procedure. In this case the sample mass of 350 mg was transferred to a Teflon perfluoroalkoxy (PFA) vessel and to which was added 3.0 ml HNO_3 conc. and 0.5 ml H_2O_2. The heating program was implemented in 4 successive steps with a total cycle of 11 min (Table 1).

Table 1. Microwave decomposition program.

Step	Time (min)	Power (W)
1	1.0	250
2	1.0	0
3	4.0	250
4	5.0	400

Masses varying from 30 to 200 mg of each SRM were transferred to the glass vials and the following procedure was applied: an aliquot of 1.0 ml of HNO_3 conc. was added to each vial containing up to 100 mg of the SRM and the heating was promoted by applying a voltage of 10 V during 150 s. For masses greater than 100 mg, 2.0 ml of HNO_3 conc. was added and the heating was promoted by applying 10 V during 240 s. The flask was carefully opened and volumes of 0.5 or 1.0 ml of H_2O_2 conc. solution were added. The same voltage was then applied during 90 s. The flask containing the decomposition mixture and the sample was positioned in the focal point of the triangular lamp arrangement. The resulting suspensions were quantitatively transferred to 25 ml volumetric flasks, without any previous centrifugation step and the volumes were made up with water.

Copper and Mn were determined by GFAAS using the standard additions method. The heating program developed is shown in Table 2. Due to their greater concentrations, Fe and Zn were determined by FAAS using air-C_2H_2 and the conditions recommended by the manufacturer[11].

Table 2. Graphite furnace heating program.

Step	Temp (°C)	Time (s)	Gas flow rate (l min^{-1})	Read
1	85	5.0	3.0	No
2	95	40.0	3.0	No
3	120	10.0	3.0	No
4	800 1000*	5.0	3.0	No
5	800 1000*	1.0	3.0	No
6	800 1000*	2.0	0.0	No
7	2300 2800*	1.1	0.0	Yes
8	2300 2800*	2.0	0.0	Yes
9	2500 2800*	2.0	3.0	No

* Temperature for Manganese

Results and Discussion

All initial studies were performed with raw bovine liver samples without any sample pre-treatment.

The first experiment involved the investigation of the effect of sample mass on the solubilization of Cu and Mn using 1.0 ml HNO_3 conc. plus 0.5 ml H_2O_2 conc. The obtained results are shown in Table 3. For sample masses less than 1000 mg there is a good agreement between the results for Cu and Mn despite a gradual trend to decreasing values. For the largest mass evaluated (1400 mg) the results for Cu and Mn were 19.4 and 9.8%, respectively, lower than the medias values of the previous analyses. In addition to the heating capacity and the efficiency of the heating transfer of the W lamps system, the decomposition of high mass samples was also affected because of the use of a constant volume of the decomposition mixture. The experiment was carried out by applying 10 V to the W lamps, which is 22% of the total power supported by the 3 lamps connected in series. According to data presented in the literature with an analogous system[10], the temperature in the focal point was 450°C when 10 V was applied. These same authors mentioned that the application of 40 V generated a temperature of 1700°C in the focal point. The temperatures were not measured, but it could be presummed that an unknown degree of overheating could happen in the focal point. It was experimentally observed that concentrated HNO_3 solutions boiled in 40 s in a closed vessel when a voltage of 10 V was applied.

Table 3. Effect of sample mass on the solubilization of Cu and Mn by infrared procedures.

Mass (mg)	Copper (μg g^{-1})	Manganese (μg g^{-1})
200	18.1 ± 0.2	2.90 ± 0.1
500	18.0 ± 1.1	2.89 ± 0.1
1000	17.9 ± 1.3	2.78 ± 0.2
1400	14.5 ± 0.1	2.58 ± 0.0

To investigate the effect of the decomposition mixture on the solubilization of the Cu and Mn, the sample mass was kept constant in 1000 mg and the proportion of HNO_3 conc. and H_2O_2 conc. was varied according to data shown in Table 4. Applying the Q test at a 95% confidence level for the results obtained for both elements it can be concluded that all results are acceptable and there is no pronounced effect of the decomposition mixture in the range evaluated. Unless when mentioned, all further experiments were carried out using 1.0 ml HNO_3 conc. and 0.5 ml H_2O_2 conc. According to the literature the use of H_2O_2 increased the concentration of oxalate generated during decomposition due to the partial decomposition of more complex organic compounds[12]. However, this is not so critical taking into account that all measurements were performed by GFAAS.

Table 4. Effect of the decomposition mixture on solubilization of Cu and Mn by infrared procedures.

HNO_3 (ml)	H_2O_2 (ml)	Copper (μg g^{-1})	Manganese (μg g^{-1})
1.0	0	16.4 ± 0.3	2.76 ± 0.03
1.0	0.5	18.7 ± 0.1	2.98 ± 0.01
1.0	1.0	16.1 ± 0.5	2.75 ± 0.01
0.5	1.0	17.9 ± 1.3	2.78 ± 0.17
1.0	1.0	16.1 ± 0.5	2.75 ± 0.01
1.5	1.0	18.3 ± 0.7	2.57 ± 0.05

The next step was the establishment of the effect caused by the heating time on the results for Mn in bovine liver. For a preliminary evaluation of the accuracy, this experiment was carried out using a mass of 30 mg of a SRM containing 10.5 ± 1.7 mg g^{-1}. It can be concluded that the solubilization of Mn occurs rapidly in this SRM and the heating time is not a critical parameter. All results shown in Table 5 with heating times varying from 2 to 15 min led to accurate results for Mn in bovine liver. All further experiments were carried out using a 2 min heating time. For larger masses, the heating time was proportionally incremented.

The content of Cu in this SRM was also measured for validation purposes and for a preliminary check of the applicability of the procedure for other elements, the contents of Fe and Zn were also determined (Table 6). Even for Fe, a difficultty soluble element[13], there is a good agreement between determined and certified values.

Table 5. Effect of heating time in the determination of Mn in bovine liver. (Certified value is 10.5 ± 1.7 μg g^{-1}, SRM 1577b, NIST).

Time (min)	Mn (μg g^{-1})
2	9.8 ± 0.2
4	9.9 ± 0.1
8	9.1 ± 0.3
10	10.1 ± 0.2
15	9.2 ± 0.2

For further evaluation of the applicability of the infrared procedure, Cu, Fe, Mn, and Zn were also determined in a botanical standard reference material (apple leaves). Botanical samples can be more difficultt to decompose than biological samples due to the formation of insoluble silicate compounds in the vegetal tissue[13]. For all elements apart from Zn, slightly lower values were determined when compared to certified values; the worst was that obtained for Fe which is not surprising for a botanical matrix owing to the formation of mixed oxides with Si that require HF for complete solubilization. Despite this small deviation between measured and certified values, Cu, Mn, and Zn results are in agreement at a 95% confidence level.

Three bovine liver samples were also decomposed adopting a microwave-assisted procedure. The results comparing this procedure and the infrared procedure for Cu and Mn are shown in Table 7. Despite an apparent positive systematic error for Cu values determined using the IR procedure, a paired t-test showed that all results for Cu and Mn are in agreement at a 95% confidence level.

All measurements were performed without any sample pre-treatment. To evaluate the effect of water content and particle sizes on the infrared decomposition procedure, one of the previous bovine liver samples was freeze-dried and Cu and Mn were determined in the resulting powder. Both decomposition procedures, *i.e.* infrared and microwaves, were implemented. Considering the results obtained and the typical water content of raw bovine liver (70%)[14], it was found a complete agreement between the results for both elements after freeze-drying or without any previous treatment was found. The results are shown in Table 8. The ratio obtained between raw and freeze-dried values for each element are close to the ratio between the raw and the freeze-dried sample masses (3.3). It can be concluded that the particle size was not so critical for bovine liver and the solubilization of the analytes was effective even for roughly cut raw samples.

Conclusions

The infra-red heating procedure was successfully applied for determination of Cu, Mn, and Zn in bovine liver and apple leaves. The procedure was also suitable for the determination of Fe in bovine liver, but the results for apple leaves were lower than expected. The behavior of different analytes present in different matrices needs to be fully evaluated to establish advantages and disadvantages of the infrared procedure. At this point, its main characteristics are the low cost and the fast sample preparation. The partial decomposition can be an obstacle for some analytical techniques of measurement. We intend to further develop this procedure as an one flask procedure for preparation of low mass samples for trace analysis. Additionally, it can be mentioned that instead of using the US$ 120.00 lamps, with the tungsten coil inserted in a gold concave structure, US$ 5.00 halogen lamps (Decostar 51, 50 W - 12 V, Osram, Germany) could be used but the heating speed is reduced 3-fold.

Table 6. Determination of Cu, Fe, Mn, and Zn in botanical and biological standard reference materials. Mean values and SDs (n = 5).

	Bovine Liver		Apple Leaves	
	Certified	Determined	Certified	Determined
Cu (mg g^{-1})	160 ± 8	155 ± 10	5.64 ± 0.24	5.17 ± 0.65
Mn (mg g^{-1})	10.5 ± 1.7	9.0 ± 0.4	54 ± 3	41 ± 2
Fe (mg g^{-1})	184 ± 5	172 ± 8	80*	42.4 ± 0.2
Zn (mg g^{-1})	127 ± 16	126 ± 19	12.5 ± 0.3	13.8 ± 0.7

*Not Certified

Table 7. Comparison of digestion methods for bovine liver samples.

Sample	Copper (μg g^{-1})		Manganese (mg g^{-1})	
	MW	IR Lamps	MW	IR Lamps
1	52.8 ± 3.8	69.7 ± 0.9	2.49 ± 0.30	2.36 ± 0.22
2	137.2 ± 7.4	148.6 ± 13.0	1.30 ± 0.06	1.34 ± 0.10
3	48.3 ± 2.6	52.6 ± 5.2	1.44 ± 0.01	1.53 ± 0.09

Table 8. Effect of water content and particle sizes on the infrared decomposition procedure.

	MW			IR Lamps		
	Raw	Freeze-dried	f	Raw	Freeze-dried	f
Cu (μg g^{-1})	48.3 ± 2.6	144.5 ± 13.8	3.0	52.6 ± 5.2	164.1 ± 4.6	3.1
Mn (μg g^{-1})	1.44 ± 0.01	4.53 ± 0.27	3.1	1.53 ± 0.09	5.10 ± 0.28	3.3

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