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Optimized microwave-assisted decomposition method for multi-element analysis of glass standard reference material and ancient glass specimens by inductively coupled plasma atomic emission spectrometry

G. Zachariadis [*], E. Dimitrakoudi, A. Anthemidis, J. Stratis

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University, Thessaloniki 54124, Greece

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Abstract

A novel microwave-assisted wet-acid decomposition method for the multi-element analysis of glass samples using inductively coupled plasma atomic emission spectrometry (ICP-AES) was developed and optimized. The SRM 621 standard reference glass material was used for this purpose, because it has similar composition with either archaeological glass specimens or common modern glasses. For the main constituents of SRM 621 (Ca, Na, Al, Fe, Mg, Ba and Ti), quality control data are given for all the examined procedures. The chemical and instrumental parameters of the method were thoroughly optimized. Thirteen acid mixtures of hydrochloric, nitric, and hydrofluoric acids in relation to two different microwave programs were examined in order to establish the most efficient protocol for the determination of metals in glass matrix. For both microwave programs, an intermediate step was employed with addition of H_3BO_3 in order to compensate the effect of HF, which was used in all protocols. The suitability of the investigated protocols was evaluated for major (Ca, Na, Al), and minor (Fe, Mg, Ba, Ti, Mn, Cu, Sb, Co, Pb) glass constituents. The analytes were determined using multi-element matrix matched standard solutions. The analytical data matrix was processed chemometrically in order to evaluate the examined protocols in terms of their accuracy, precision and sensitivity, and eventually select the most efficient method for ancient glass. ICP-AES parameters such as spectral line, RF power and sample flow rate were optimized using the proposed protocol. Finally, the optimum method was successfully applied to the analysis of a number of ancient glass fragments.

Keywords: Microwave decomposition; Glass analysis; Inductively coupled plasma atomic emission spectrometry; Metals; Ancient glass

1. Introduction

A very important part of provenance and characterization studies in the field of archaeometry is the elemental chemical analysis because it provides information about the raw materials used and permits conclusions about the recipe employed. A number of destructive and non-destructive instrumental multi-element techniques are available for the analysis of glasses, ceramics and other silicate matrices for archaeological purposes. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a widely used technique for the above samples [1–5] as it is sensitive, accurate and with low detection limits. X-ray fluorescence (XRF), proton induced X-ray emission (PIXE) [6,7], laser induced breakdown spectroscopy (LIBS) [8] or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [9] are alternative techniques for the non-destructive or semi-destructive analysis of archaeological specimens with the advantage of limited sample deterioration.

Due to the fact that ICP-AES uses mainly liquid samples, an effective and convenient decomposition method is usually necessary. Destructive procedures like wet-acid decomposition in open vessels or alkaline fusion [10] are commonly applied to the analysis of silicate matrices like ancient glasses. The above decomposition methods, when conventional heating is employed, have some serious disadvantages like long reaction time, incomplete dissolution of silicate matrix, sample contamination and losses of volatile elements. Many of these disadvantages can be overcome using microwave-assisted wet-

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[*] Corresponding author.
E-mail address: zacharia@chem.auth.gr (G. Zachariadis).

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acid decomposition in closed-pressurized vessels in presence of an appropriate acid mixture containing hydrofluoric and boric acid or alternatively HBF_4 [11]. However, although several microwave-assisted decomposition procedures have been reported for various silicate matrices like soils, rocks and sediments [12–15], the use of microwaves for the analysis of glasses and ceramics is rather limited in literature, especially for samples of archaeological interest. In this field there are very few studies which use microwave-assisted decomposition for sample preparation [4,16] and to the best of our knowledge, relevant experimental data for effective acid mixtures and optimized microwave protocols are not readily available for ancient glass matrices.

The aim of the present work was to develop a method for microwave-assisted wet-acid decomposition of glass matrix, suitable for subsequent analysis by ICP-AES. For this purpose, a number of 13 acid mixtures containing HCl, HNO_3 and HF were examined for their effectiveness in relation to 2 different microwave programs for pressure and temperature. Consequently, 26 microwave-assisted decomposition protocols were tested to a standard glass reference material SRM 621 (NIST) in order to determine the most accurate and efficient protocol for the simultaneous multi-element analysis. The accuracy was evaluated by comparing the mean experimental concentrations with the corresponding certified values of the SRM material. In addition, the slopes of the calibration curves were used as a reliable criterion to evaluate the sensitivity, while the relative errors were used to estimate the accuracy of each procedure. Furthermore, similarities and dissimilarities of the protocols were evaluated by applying cluster analysis. Finally, the most efficient method was applied to the analysis of ancient glass fragments from a byzantine excavation in Greece.

2. Experimental

2.1. Instrumentation

All decompositions were performed in a MARS 5 Microwave Sample Preparation System (CEM, USA, 1200 W) equipped with a 14-vessels rotor. Samples were placed in high-pressure closed (100 ml, HP-500 Plus type, P_{max} 350 psi, T_{max} 210 °C) PTFE vessels. A Perkin Elmer Optima 3100 XL inductively coupled plasma atomic emission spectrometer (ICP-AES) by axial viewing configuration of the atmospheric pressure argon plasma was used throughout. The spectrometer was equipped with a 40 MHz, free-running RF generator, a fassel-type alumina torch injector, a gem tip cross-flow nebulizer and a scott double-pass spray chamber. The spectrometer consisted from an echelle grating polychromator with a 0.006 nm resolution at 200 nm and a segmented-array charge-coupled detector. Two spectral lines for quantitation of each element—Al: 308.215 and 237.313 nm; Fe: 238.204 and 239.562 nm; Ca: 317.933 and 396.847 nm; Mg: 279.077 and 280.271 nm; Ti: 334.94 and 336.121 nm; Ba: 233.527 and 230.425 nm; Na: 330.237 and 330.298 nm; Mn: 257.610 and 259.372 nm; Cu: 324.752 and 224.7 nm; Co: 228.616 and 238.892 nm; Sb: 206.836 and 217.582 nm; Pb: 220.353 and 261.418 nm.

2.2. Reagents and standards

All chemical reagents were of analytical reagent grade. In particular, the following reagents were used: HNO_3 65% (Merck), HCl 37% (Riedel-de Haen), HF 40% (Merck, Suprapur), H_3BO_3 (Merck, Suprapur). For the preparation of all solutions doubly deionized water (ASTM Type I water, 18.2 MΩ cm), was used. Matrix-matched calibration standards were prepared from stock solutions (1000 mg l^{-1}) (Fluka) in 0.5 mol l^{-1} HNO_3 (Merck), according to the procedures described below.

The standard reference material SRM 621 (NIST), which was used for evaluation of the microwave decomposition protocols, has a chemical composition very close to the archaeological soda-lime glass samples concerning the elements: Al, Ca, Mg, Fe and Na. Soda-lime is the most common type of byzantine and medieval glasses found in Mediterranean basin. The composition and the uncertainty values for the SRM 621 are given in Ref. [1]. The SRM 621, was finely powdered in a mortar to <60 mesh and dried for 1 h at 120 °C. Accurately weighed amounts of 0.1 g SRM 621 were subjected to the examined decomposition protocols as described in Section 2.4.

All artificial working standard solutions were decomposed according to the studied microwave decomposition protocols applied to SRM 621 sub-samples, in order to compensate possible losses of volatiles. Six working standard solutions containing all the analytes were prepared according to the expected concentration of the elements: Na, Ca, Al, Mg, Ba, Fe, Ti which are the main components of SRM 621. The multi-element standard solutions were prepared in a way that matches the matrix of the solutions obtained after complete decomposition of 0.1 g of the sample. For this reason, a suitable amount of SiO_2 was added to the standard solutions into the decomposition vessels together with the standard solutions. The matrix-matching approach by dissolving an equivalent amount of SiO_2 and adding variable concentrations of the other elements ensures that even the remaining quantity of not-reacted HF resembles that of the real glass samples. However, due to the fact that archaeological soda-lime glasses usually contain some other elements like Sb, Pb, Cu, Co and Mn, these analytes were also added, although they do not appear in the standard reference material SRM 621. Finally, for all the microwave decomposition protocols, individual calibration curves ($n = 6$) for ICP-AES were obtained for the two spectral lines of each analyte.

2.3. Acid mixtures

Glass or glassy matrices are difficult to be dissolved by common rapid dissolution procedures due to the silicate matrix. One of the most common approaches involves the acid attack of the sample by a mixture of acids, definitely containing hydrofluoric acid, or alternatively, the alkaline fusion by using sodium or lithium fluxes. In this study various acid mixtures of concentrated HNO_3, HCl and HF (Table 1), were compared to investigate the most efficient combination for the extraction of

Table 1
Acid mixtures for microwave-assisted decomposition procedures for SRM 621

Mixture number	HCl (ml)	HNO_3 (ml)	HF (ml)
1	–	3.0	3.0
2	–	2.0	4.0
3	–	1.5	4.5
4	2.0	2.0	2.0
5	1.5	1.5	3.0
6	1.2	1.2	3.6
7	3.0	1.5	1.5
8	2.4	1.2	2.4
9	2.0	1.0	3.0
10	3.0	1.0	2.0
11	1.0	3.0	2.0
12	3.0	–	3.0
13	1.5	3.0	1.5

metals from glass material, at the best decomposition conditions. In all cases, the total volume of acids into the PTFE vessel was fixed to 6 ml.

2.4. Microwave-assisted decomposition

Amounts of 0.1 g of the SRM 621 were accurately weighted into high-pressure closed teflon decomposition vessels. Then, 2 ml de-ionized water and 6 ml of acid mixture were added carefully. The vessels were gently shaken and sealed. A total of eight sub-samples were evenly spaced on the microwave turntable. The final mixture was diluted to 100 ml. The vessels were washed by 5 min heating in microwave oven at 1200 W in presence of 30 ml 0.5 mol l^{-1} HNO_3.

Two different heating programs were examined. The first microwave program consisted of four stages (I–IV) and was labeled as “*A*”. The second microwave program consisted of two stages (I and II) and was labeled as “*B*”. The setting conditions of the two programs used in the present study are given in Table 2. Microwave heating programs “*A*” and “*B*” were applied in combination with the various acid mixtures and finally 26 methods were investigated. Each protocol was labeled from the acid mixture that was used for the decomposition as reported in Table 1, and the microwave program which was applied, e.g. 4A, 5B, etc.

Temperature and pressure sensors were attached to a control vessel in order to monitor and record the reaction conditions continuously during the decomposition. The decompositions were pressure-controlled and the heating of the sample was interrupted when P_{max} was reached in the vessel. The internal temperature was monitored with a sensor unit (IR temperature unit) and ranged between 180 and 185 °C during the microwave heating programs. At the end of the stage III of program A and the stage I of program B, the vessels were cooled to room temperature and removed from the microwave system. After cooling, 20 ml saturated solution of H_3BO_3 was added to permit the complexation of fluoride ions and to dissolve the formed fluoride salts. A final lower pressure heating stage was used for both microwave programs (stage IV for A and stage II for B). Instead of using HF followed by a separate step of H_3BO_3, one could use HBF_4 for simultaneous reaction of both acids, however, considering the fact that fluoroboric acid action is less efficient for quartz [11]. Reagent and procedural blanks were obtained, and three sub-samples were analysed in all cases. The vessels were cooled again at room temperature, and the final sample solutions was transferred to a polyethylene 100 ml volumetric flask and diluted with de-ionized water.

Table 2
Microwave heating programs studied for wet-acid decomposition

Stage	Power (W)	Pressure (psi)	Time (min)
Program “A”			
I	500	50	7
II	550	100	7
III	600	100	5
IV	630	50	5
Program “B”			
I	535	80	18
II	630	50	5

3. Results and discussion

3.1. Optimization of decomposition protocols

The standard reference glass material SRM 621 was decomposed by the 13 examined acid mixtures in relation to two different microwave programs for each mixture, as described above. The analytical results obtained from the ICP-AES analysis are listed in Table 3, for microwave programs “A” and “B”, respectively. For each metal, expressed as the corresponding oxide, the mean concentration found ($\bar{x}$), and the relative standard deviation (R.S.D.%, $n = 3$) were calculated separately for the two emission lines, except Ca and Ba, for which quantitation was achieved only in one spectral line. Chemical composition is expressed as oxide concentration in % m/m.

The calculated relative errors (e_r) were used to evaluate the accuracy. These values are based on the difference between the mean experimental concentration ($\bar{x}$) and the certified value (μ) of each analyte. For all analytes, two different spectral lines were evaluated, except for Ca and Ba, for which only one spectral line was evaluated because Ca at 396.847 nm and Ba at 230.425 nm could not be quantified. In Fig. 1, for comparative purposes the absolute values of the percentage relative errors for some analytes are presented concerning microwave program “A”. It is clearly demonstrated that some protocols like 5A, 13A and 2A are definitely not suitable, while others are very efficient, like 8A and 3A.

The results were further evaluated in respect to the relative errors. For this purpose the null hypothesis at 95 % confidence level was used. When the above difference is smaller than a critical value at the defined confidence level the null hypothesis stands, and consequently no evidence exist for significant difference between the mean experimental concentration and the certified concentration (Student’s *t*-test). Table 4 lists the results of Student’s *t*-test (95%) for the significance of differences between mean experimental and certified concentrations for each element and for all the examined protocols using the microwave programs “A” and “B”, respectively. These results

Table 3

Analytical results (mean values in % m/m, R.S.D.%, $n = 3$) obtained for SRM 621 using the investigated decomposition protocols and microwave programs A and B

	Al_2O_3 (certified 2.76 ± 0.04)		Fe_2O_3 (certified 0.04 ± 0.003)		CaO (certified 10.71 ± 0.05)	MgO (certified 0.27 ± 0.03)		TiO_2 (certified 0.014 ± 0.003)		BaO (certified 0.12 ± 0.05)	Na_2O (certified 12.74 ± 0.05)	
	λ = 308.215 nm	λ = 237.313 nm	λ = 238.204 nm	λ = 239.562 nm	λ = 317.933 nm	λ = 279.077 nm	λ = 280.271 nm	λ = 334.940 nm	λ = 336.121 nm	λ = 233.527 nm	λ = 330.237 nm	λ = 330.298 nm
1A	1.98	2.85	0.03	0.03	11.28	0.22	0.22	0.009	0.009	0.13	12.55	13.51
R.S.D.	6.3	1.0	2.9	3.2	1.7	1.6	1.1	1.6	1.6	2.0	0.4	5.4
2A	1.32	1.34	. .	. .	7.11	0.08	0.08	0.007	0.007	0.09	8.46	8.40
R.S.D.	0.2	0.4			0.2	6	0.1	4.2	2	0.4	0.4	0.8
3A	2.78	2.72	. .	0.025	10.8	0.15	0.15	0.011	0.014	0.10	12.16	12.32
R.S.D.	8.6	8.3		12.5	8.1	0.7	1.4	8.5	7.4	8.1	8.5	8.5
4A	. .	2.65	0.01	0.010	10.62	0.11	0.11	0.012	. .	0.09	12.08	11.44
R.S.D.		0.3	9.3	10.5	1.3	0.6	1.0	0.7		0.6	0.7	7.0
5A	4.72	4.52	. .	0.031	17.73	0.09	0.10	0.017	0.022	0.16	20.56	20.79
R.S.D.	3.6	1.6		9.9	3.6	10.4	9.8	9.8	4.9	3.1	1.8	0.2
6A	. .	2.7	0.03	0.045	10.43	0.19	0.18	0.012	. .	0.1	11.87	13.13
R.S.D.		4.3	9.5	7.5	5.6	1.5	1.7	7.2		4.6	5.2	4.2
7A	2.60	2.73	0.03	0.03	10.54	0.16	0.15	0.014	0.011	0.10	12.74	12.77
R.S.D.	0.5	1.3	6.4	4.7	1.4	1.1	1.8	2.3	3.7	4.0	4.0	1.7
8A	2.71	2.71	0.040	0.044	10.6	0.21	0.19	0.013	0.014	0.11	11.96	11.98
R.S.D.	1.3	1.4	4.4	3.6	2.1	1.4	1.1	2.7	1.7	3.1	1.5	2.8
9A	2.71	2.72	0.02	0.030	10.77	0.18	0.19	0.013	0.013	0.10	12.25	12.20
R.S.D.	1.6	0.8	7.7	3.3	1.4	1.1	0.8	0.8	0.6	1.1	0.8	0.9
10A	2.62	2.58	0.03	0.031	9.47	0.13	0.13	0.012	0.012	0.09	11.56	11.48
R.S.D.	2.2	0.8	3.7	1.7	1.8	0.9	1.4	2.0	2.6	1.4	0.9	0.3
11A	2.87	2.82	0.02	0.030	11.32	0.16	0.16	0.013	0.014	0.11	12.70	12.84
R.S.D.	3.3	3.5	5.3	2.4	2.2	2.5	2.4	5.0	1.8	3.2	3.8	3.6
12A	2.6	2.6	0.02	0.030	10.28	0.16	0.17	0.012	0.012	0.10	11.8	11.6
R.S.D.	0.2	0.5	3.4	2.6	0.4	1.2	1.2	1.7	0.3	0.4	1.1	3.2
13A	3.22	3.06	0.03	0.030	11.78	0.16	0.16	0.014	0.015	0.11	13.81	13.98
R.S.D.	3.7	1.1	4.3	1.91	1.1	3.1	2.5	4.1	3.5	1.2	1.2	1.8
1B	. .	3.00	0.02	0.02	11.95	0.17	0.17	0.013	. .	0.12	13.40	14.6
R.S.D.		0.6	14.1	10.3	1.1	0.7	0.9	2.43		1.3	0.9	1.4
2B	1.43	1.44	. .	0.03	7.56	0.07	0.07	0.008	0.008	0.09	9.02	8.95
R.S.D.	1.64	1.62		4.7	2.1	3.4	2.95	4.8	2.0	1.9	1.9	2.4
3B	2.7	2.7	. .	0.03	10.78	0.17	0.17	0.011	0.013	0.10	12.17	12.23
R.S.D.	6.1	6.5		8.1	5.8	1.6	1.3	11.1	6.5	6.3	6.6	6.7
4B	2.93	2.63	0.02	0.03	10.41	0.12	0.12	. .	0.015	0.10	11.59	12.05
R.S.D.	3.0	0.7	5.5	2.5	1.0	1.3	0.5		4.0	1.0	0.5	2.3
5B	2.70	2.69	0.02	0.03	10.68	0.12	0.12	0.012	0.013	0.10	12.02	12.22
R.S.D.	3.1	2.3	8.3	5.7	3.3	3.4	4.0	1.4	4.3	2.8	1.9	3.0
6B	. .	2.85	0.02	0.03	11.19	0.16	0.16	. .	. .	0.11	. .	13.40
R.S.D.		3.4	3.6	5.4	0.3	1.7	1.9			3.4		5.9

7B	2.70	2.66	0.02	0.03	9.81	0.17	0.17	0.012	0.012	0.09	12.0	11.8
R.S.D.	3.7	2.8	28.3	17.7	1.6	1.0	1.5	1.2	2.7	1.3	3.5	5.5
8B	2.71	2.72	0.03	0.03	10.77	0.19	0.20	0.013	0.013	0.10	12.25	12.2
R.S.D.	0.7	0.8	7.65	3.3	1.4	1.1	1.0	0.8	0.6	1.14	0.8	0.9
9B	2.93	2.92	0.04	0.04	11.76	0.20	0.20	0.013	0.014	0.11	13.1	13.16
R.S.D.	1.7	1.0	2.2	1.6	1.5	1.5	1.8	1.6	1.6	1.5	0.9	1.3
10B	2.58	2.55	0.03	0.04	9.20	0.15	0.15	0.012	0.012	0.09	11.40	11.47
R.S.D.	3.0	3.0	9.4	6.3	4.8	0.8	0.7	5.9	4.2	3.8	3.2	2.8
11B	2.73	2.79	0.03	0.03	10.90	0.16	0.17	0.013	0.013	0.10	12.54	12.32
R.S.D.	1.9	1.6	6.6	3.3	1.1	1.0	0.7	1.9	1.8	1.7	1.9	1.2
12B	2.54	2.59	0.02	0.03	10.24	0.14	0.13	0.012	0.012	0.10	11.6	11.5
R.S.D.	1.4	1.1	5.5	4	1.2	1.5	1.5	0.6	2.7	1.6	0.9	1.5
13B	1.60	1.54	0.02	0.02	8.08	0.12	0.12	0.007	0.009	0.10	9.54	9.77
R.S.D.	6.6	5.0	10.3	4.7	5.8	1.7	2.5	5.2	7.3	5.3	5.1	6.4

“. .”: not quantified.

are discussed below in detail in order to determine the most effective method.

As it is shown in Table 4, microwave program “A” is the most efficient for the extraction of all the analytes from reference glass material SRM 621, and the most effective protocol is 8A (2.4 ml HCl:1.2 ml HNO_3:2.4 ml HF, microwave heating program A). According to microwave program B, the most effective protocol is 3B. In program A, the pressure and the power were increased gradually from a lower level to a higher one, in contrast to program B, where the power and the pressure were kept at a medium level. The starting low temperature step of program A (power 500 W, pressure 50 psi) is necessary for regular breaking down the glassy structure and for diffusion of the reactants toward one another through the reaction mixture. Also this step limits the losses of the volatile compounds which are formed during the decomposition.

Compositional data from the 26 protocols were further subjected to hierarchical cluster analysis using complete linkage and Euclidean distances, in order to confirm the differentiation of the most efficient ones against the others. A representative dendrogram is given in Fig. 2.

As can be seen in Fig. 2, the most efficient procedures 8A, 3A, 3B are members of initial close clusters, and form a larger cluster. This result confirms the experimental observations described above concerning the performance of the three most efficient procedures. Also a characteristic differentiation between the group of (5A, 5B, 2A, 2B, 13B) and the group of (1B, 13A, 1A) with the other procedures is observed. As it is mentioned above, these procedures are inefficient for the accurate determination of most analytes (see also Table 3). The Euclidean distances between the most efficient procedures are small while the less efficient presented in most cases much different values.

For 8A protocol the null hypothesis stands for six elements which are: Al, Ti, Ca, Fe, Ba, and Na, but not in all spectral lines. For these elements the precision (relative standard deviation, R.S.D.) ranged between 1.3 and 3.6% and the relative errors between 1.4 and 6.7%.

Efficient decomposition was also achieved in a lesser extend with 3A, 3B protocols. In particular, for 3A and 3B the null hypothesis stands also for five elements which are the same for both protocols. These elements are: Al, Na at both spectral lines, Ca at 317.933 nm, Ti at 336.121 nm, Ba at 233.527 nm. For 3A the precision ranged between 7.4 and 8.6% and the relative error between 0.6 and 4.5% except for Ba (14.1%). For 3B protocol, the precision ranged between 5.8 and 6.6% and the relative error range between 0.4 and 6.5% except for Ba (14%). The difference between 3A and 3B is just the heating program, while the acid mixture is the same. The high relative error values observed for Fe with 3A and 3B, 36.6 and 28.8%, respectively, showed that the presence of HCl had a positive influence in the release of Fe from the glass.

For 6A the null hypothesis stands for five elements that are: Al at 237.313 nm, Fe, Na at both spectral lines, Ca at 317.933 nm, Ti at 334.940 nm. The precision of the determination ranged between 4.3 and 7.5%. The relative error is <10% for Al, Ca, Na, whereas for Fe at 239.562 nm was 10.6% and for Ti at 334.94 nm was 15.4%, respectively.

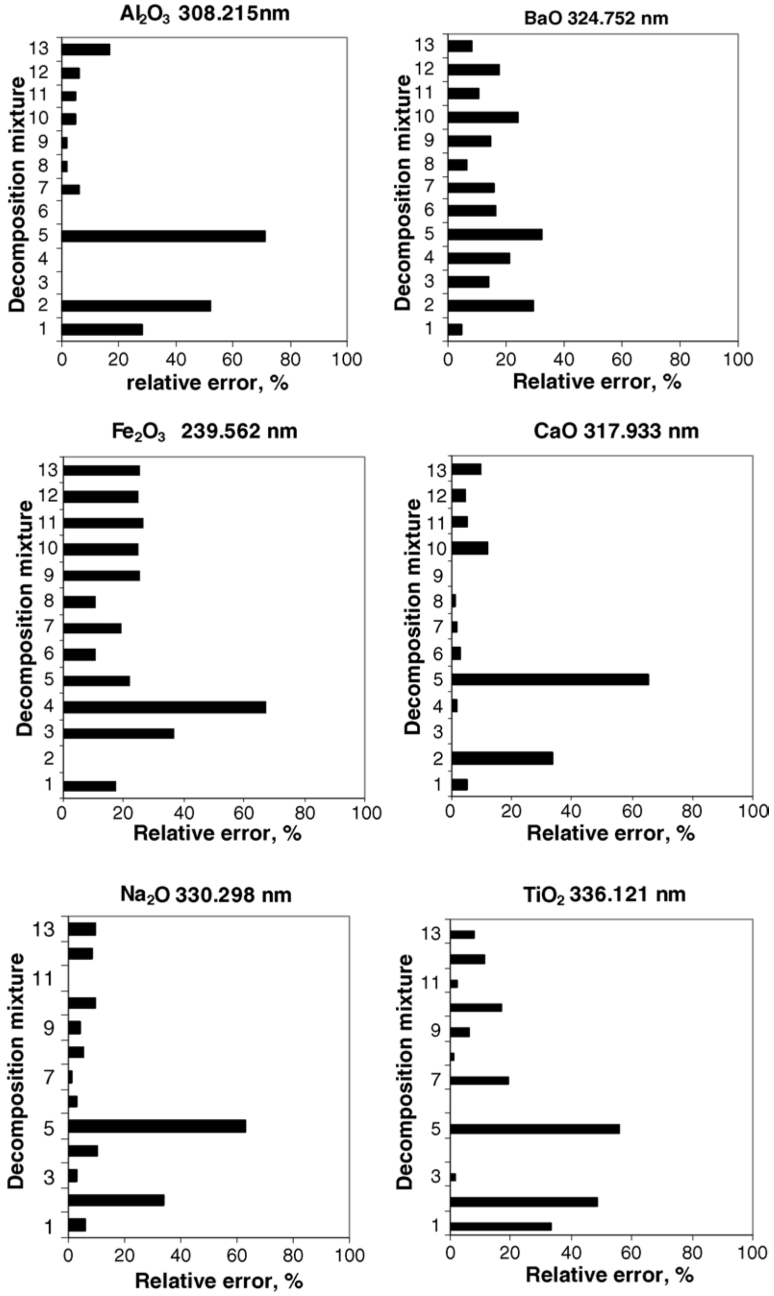

Fig. 1. Relative errors calculated for the 13 decomposition protocols, using microwave program “A”.

The presence of hydrofluoric acid in the decomposition mixtures was necessary to break down the silicate matrix. Al, Ca, Ti and Na were determined with 8A, 3A, 3B and 6A protocols but Fe was efficiently quantitated only with 8A, probably due to the increased concentration of HCl in the acid mixture. Also, the lower relative errors for Mg were observed for 8A method. Ba was determined efficiently with 3A, 3B, 8A methods, but the accuracy is better for 8A method. According to all the above results, the 8A protocol was proved as the optimum for the most efficient decomposition of the glass matrix. Consequently, based on this protocol the whole method was subjected to further optimization of the instrumental settings of the plasma spectrometer, as it is described below.

3.2. Optimization of ICP-AES instrumental parameters

3.2.1. Optimization of plasma parameters

The sample flow rate is a critical parameter because it largely determines the residence time of the analyte species in the center of the plasma torch. The higher flow rate the more amount of the sample solution to be atomized into the plasma. Consequently, for analytes which emit strong atomic lines, a faster flow rate might be used. The incident RF power effects the atom excitation according to the nature of the analyte species. The more power is applied to the plasma, the hotter the plasma gets. Consequently, for analytes that require more energy for excitation and ionization, a higher power would provide greater sensitiv-

Table 4
Results of Student's *t*-test at 95% confidence level for the significance of differences between certified and mean experimental concentrations obtained for each analyte using microwave programs A and B

Component	Wavelength (nm)	Decomposition protocol[a]												
		1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A
Al_2O_3	308.215	+	+	–	..	+	..	+	–	–	–	–	+	+
	237.313	+	+	–	+	+	–	–	–	–	+	–	+	+
Fe_2O_3	238.204	+	..	..	+	..	–	+	–	+	+	+	+	+
	239.562	+	..	..	+	+	–	+	–	+	+	+	+	+
CaO	317.933	+	+	–	+	+	–	–	–	–	+	–	+	+
MgO	279.077	+	+	+	+	+	+	+	+	+	+	+	+	+
	280.271	–	+	+	+	+	+	+	–	+	+	+	+	+
TiO_2	334.940	+	+	+	+	–	–	–	–	+	+	–	+	–
	336.121	+	+	–	..	+	..	+	–	+	+	–	+	–
BaO	233.527	–	+	–	+	+	+	+	–	+	+	+	+	+
Na_2O	330.237	+	+	–	+	+	–	–	+	+	+	–	+	+
	330.298	–	+	–	–	+	–	+	–	+	+	–	+	+
		1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B
Al_2O_3	308.215	..	+	–	–	–	..	–	–	+	–	–	+	+
	237.313	+	+	–	+	–	–	+	–	+	+	–	+	+
Fe_2O_3	238.204	+	..	..	+	+	+	+	+	+	+	+	+	+
	239.562	+	+	+	+	+	+	+	+	–	–	+	+	+
CaO	317.933	+	+	–	+	–	+	+	–	+	+	–	+	+
MgO	279.077	+	+	+	+	+	+	+	+	–	+	+	+	+
	280.271	+	+	+	+	+	+	+	+	–	+	+	+	+
TiO_2	334.940	–	+	+	..	+	..	+	+	–	+	–	+	+
	336.121	..	+	–	–	–	+	+	..	–	–	–	+	+
BaO	233.527	+	+	–	+	+	+	+	+	+	+	+	+	+
Na_2O	330.237	+	+	–	+	+	–	–	+	+	+	–	+	+
	330.298	+	+	–	+	–	–	–	+	+	+	+	+	+

[a] Cases of non-significant differences are denoted with "–" and cases of significant differences are noted with "+"; ".." means "not quantified.

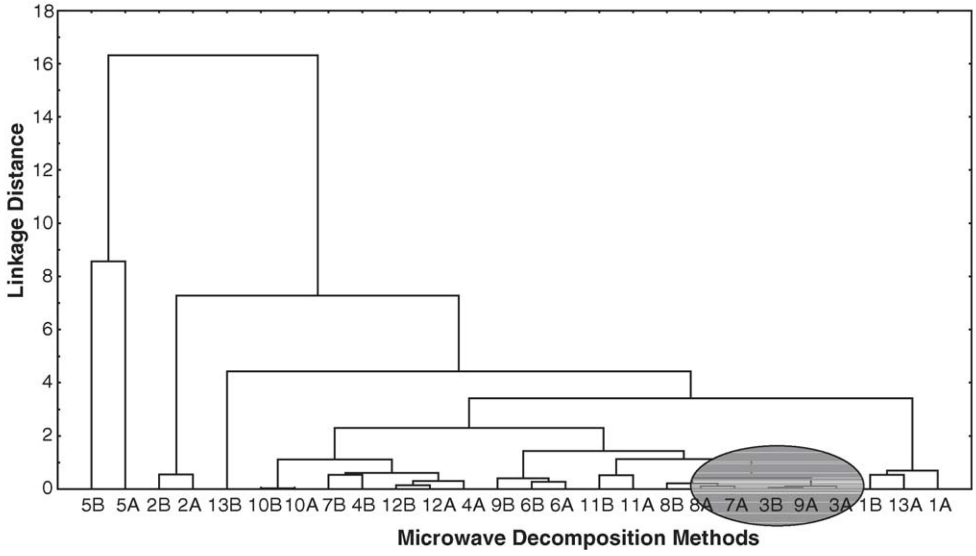

Fig. 2. Hierarchical clustering dendrogram for the 26 decomposition protocols using complete linkage and Euclidean distances.

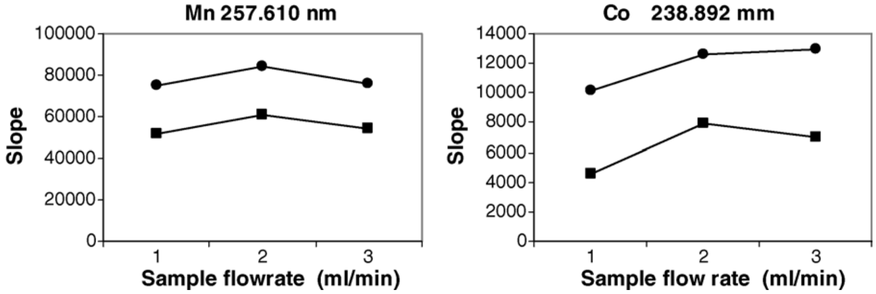

Fig. 3. Effect of the sample flow rate and the RF power of the ICP-AES on the sensitivity (expressed by slope of calibration curve) of the determination of Mn and Co in glass standard reference material SRM 621. RF power: (■) 1300 W; (●) 1500 W.

ity, while for easy excited analytes, lower power would increase their sensitivity.

The influence of sample flow rate and RF power on the sensitivity was studied using the calibration curves which were obtained from six standard solutions varying the sample flow rate in the range 1–3 ml $\min^{-1}$ and the RF power between 1300 and 1500 W, respectively. The results of the regression analysis (slopes) indicate that the sensitivity of the determinations is higher for RF power at 1500 W and for sample flow rate at 2 ml $\min^{-1}$ as it is shown in Fig. 3.

In particular for all analytes, with RF power at 1300 W, the higher sensitivity was observed for sample flow rate 2 ml $\min^{-1}$. With RF power at 1500 W the sensitivity is also higher for sample flow rate at 2 ml $\min^{-1}$ for the analytes: Al (308.215 nm), Ba (233.527 nm), Mn (257.610 nm), Cu (324.752 nm), while for Ca (317.933 nm), Na (330.298 nm), Co (238.892 nm) increases significantly for sample flow rate 1–2 ml $\min^{-1}$ but for 2–3 ml $\min^{-1}$ no further significant change is observed. For Ti (336.121 nm), Fe (239.562 nm) and Mg (280.271 nm) the sensitivity decreases for sample flow rate 2–3 ml $\min^{-1}$.

Finally, the optimum operating conditions of ICP-AES were: RF power 1500 W; sample flow rate 2 ml $\min^{-1}$. Finally, these were applied to the analysis of archaeological samples, as it is discussed in Section 3.3.

3.2.2. *Sensitivity check and spectral line selection*

The sensitivity of the characteristic spectral lines of the analytes is likely to be affected by the matrix of the resulting solution after the various decomposition procedures. Thus, at this step, the best spectral line should be primarily evaluated according to the overall sensitivity obtained. The results of the regression analysis for the most efficient protocol 8A are given in Table 5, including for each element only the spectral lines where quantitation was achieved.

The slopes of the calculated regression lines and the corresponding confidence intervals at 95% confidence level are listed. The sensitivity of determination of each chemical element at a specific spectral line is expressed by the slope of the linear regression equation (cps mg^{-1} l).

The higher sensitivities for 8A protocol were observed at the following spectral lines: Al at 308.215 nm, Fe at 239.562 nm, Ca at 317.933 nm, Mg at 280.271 nm, Ti at 336.121 nm, Ba at 233.527 nm, Mn at 257.610 nm, Cu at 324.752 nm, Co at 238.892, Pb at 261.418 nm. The sensitivity for Na and Sb was practically at the same level for both spectral lines, but a little higher is observed at Na 330.298 nm and at Sb 206.836 nm. The correlation coefficient for the majority of calibration curves was >0.998 showing good linearity through the studied concentration range. Consequently, the above spectral lines are recommended as optimum for the proposed method.

3.3. *Analysis of archaeological samples*

Ancient glass fragments were found in a byzantine excavation in Thessaloniki (Greece). They were analysed in triplicate, following the 8A protocol and the optimum conditions of the proposed microwave-assisted decomposition method, as described in Section 2.4. The results are listed in Table 6. Although all specimens were found in the same excavation, some of them showed different composition, like G-1-3 which was found to contain higher concentration of Fe, Mg, Ba, Na and Mn, than the other specimens.

Table 5
Slopes ± 95% confidence intervals (c.i.) and correlation coefficients of the regression equations for 8A protocol of glass decomposition

Element	Wavelength (nm)	Slope ± c.i.	*r*
Al	308.215	6772 ± 1668	0.9977
Al	237.313	292 ± 41	0.9899
Fe	238.204	1053 ± 460	0.9899
Fe	239.562	45910 ± 20090	0.9900
Ca	317.933	17608 ± 375	0.9999
Mg	279.077	536 ± 106	0.9975
Mg	280.271	325612 ± 61188	0.9980
Ti	334.940	2632 ± 632	0.9999
Ti	336.121	141105 ± 24815	0.9985
Ba	233.527	14152 ± 218	0.9999
Na	330.237	119 ± 47	0.9915
Na	330.298	146 ± 37	0.9985
Mn	257.610	92646 ± 2546	0.9999
Mn	259.372	42695 ± 2181	0.9999
Sb	206.836	385 ± 64	0.9985
Sb	217.582	314 ± 68	0.9999
Cu	324.752	20265 ± 1165	0.9995
Cu	224.700	1703 ± 68	0.9999
Co	238.892	13060 ± 298	0.9999
Pb	261.418	588 ± 205	0.9935

Table 6
Analysis of archaeological glass specimens (mean ± S.D., $n = 3$)

Sample	Al_2O_3 (mg kg^{-1})	Fe_2O_3 (mg kg^{-1})	CaO (mg kg^{-1})	MgO (mg kg^{-1})	TiO_2 (mg kg^{-1})	BaO (mg kg^{-1})	Na_2O (mg kg^{-1})	MnO (mg kg^{-1})	CuO (mg kg^{-1})	PbO (mg kg^{-1})
G-1-3	16133 ± 330	6853 ± 393	47709 ± 1242	5552 ± 876	868 ± 25	311 ± 44	83534 ± 2758	3055 ± 267	2185 ± 355	1862 ± 134
G-1-4	19666 ± 475	3873 ± 443	58243 ± 2482	3909 ± 308	569 ± 70	304 ± 22	63885 ± 3127	2230 ± 244	3115 ± 216	924 ± 82
G-1-5	11455 ± 668	3916 ± 232	44006 ± 1770	2632 ± 207	358 ± 13	157 ± 11	62648 ± 5933	1736 ± 202	1874 ± 352	1417 ± 90
G-1-6	20385 ± 1211	3678 ± 169	55395 ± 3499	4266 ± 279	1009 ± 25	242 ± 19	47856 ± 2089	1341 ± 171	3237 ± 159	2404 ± 124
G-1-7	14259 ± 1036	2982 ± 124	41233 ± 1589	2522 ± 97	444 ± 39	158 ± 13	53453 ± 2641	1527 ± 297	1280 ± 109	1220 ± 205

4. Conclusions

The developed microwave-assisted wet-acid decomposition method was proved efficient for the quantitative determination of major and minor constituents in standard reference glass material SRM 621. The investigated method presented good accuracy, precision, sensitivity and also speed and safety, as compared to conventional decomposition techniques of glass materials analysis. Although the recommended method is referred to the specific sample matrix, it is readily applicable to other glass materials of archaeological origin. The use of microwave heating in closed vessels accelerates the procedure and enhances the decomposition strength of the examined acid mixtures. The standard glass SRM 621 was decomposed successfully using acid mixture of $HCl + HNO_3 + HF$ and a four-stage microwave program, allowing determination of all the examined analytes. The presence of HF and HNO_3 in the acid mixture is necessary for the decomposition of glass matrix and determination of the analytes, while the use of H_3BO_3 in a separate stage of the microwave decomposition is necessary for the dissolution of the produced fluoride salts. The gradient increase of the power and the pressure during the microwave procedure were found to ensure the most efficient decomposition conditions for this material. The proposed method could be adapted to the multi-element analysis of ancient glass specimens and also can be applied to common modern glass analysis of similar composition.

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