RESIDUES AND TRACE ELEMENTS

Determination of Nine Elements in Sherry Wine by Inductively Coupled Plasma-Atomic Emission Spectrometry

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A quick and simple method was developed to analyze various "fino" sherry wines for routine determination of Al, Ca, Cu, Fe, K, Mg, Mn, Na, and Zn content. The analysis involved heating the wine sample in an oven at 80°C to evaporate the ethanol, followed by sequential determination of the elements by inductively coupled plasma-atomic emission spectrometry. The following metal concentrations (mg/L) were obtained: Al, 1.02–4.06; Ca, 85.00–150.00; Cu, 0.06–1.62; Fe, 2.19–4.91; K, 435.02–651.65; Mg, 79.1–108.57; Mn, 0.37–2.13; Na, 27.09–54.26; and Zn, 0.12–5.08. Mean recoveries of elements from fortified wines were 101.6% for Al, 103.6% for Ca, 97.4% for Cu, 100.3% for Fe, 100.7% for K, 103.6% for Mg, 99.1% for Mn, 105.7% for Na, and 99.99% for Zn. The estimated detection limits were 15.2 μg Al/L, 39.9 μg Ca/L, 20.1 μg Cu/L, 19.1 μg Fe/L, 116.4 μg K/L, 20.3 μg Mg/L, 20.2 μg Mn/L, 34.6 μg Na/L, and 25.4 μg Zn/L. The repeatability relative standard deviation ranged from 1.1 (Mg) to 5.3% (Na), and the reproducibility relative standard deviation ranged from 2.0 (Mg) to 9.3% (Al). The results were compared with those obtained by flame atomic absorption spectrometry and, for Al, by graphite furnace atomic absorption spectrometry. By the method for regression lines we demonstrated that no differences in concentrations were obtained for any of the elements assayed. The proposed method is rapid and simple, needs only a small amount of sample, and has acceptable analytical characteristics.

Methods to determine the metal content of wine are important because of the needs of the wine industry and toxicological implications. Metals can affect the entire wine-making process, from vine growing to the fermentation and aging of wine, mainly through their influence on the organoleptic properties of the finished product (1).

Several elements in the finished wine influence both its stability and its color and clarity. During the wine-making process, iron may form insoluble precipitates (as phosphates) or colloidal forms which flocculate and give an undesirable turbid aspect (2). Calcium and potassium produce precipitates due to the formation of tartaric salts (3). Aluminum (4) and copper are also responsible for turbidity and unfavorable flavor changes. Zinc, magnesium, and sodium are responsible for undesirable flavors in wine, and potassium levels determine whether the wine will taste acidic or insipid (5). Finally, manganese, which is present in wines at very low concentrations, affects the fermentation process (6) and is characteristic of the production region and the dithiocarbamate fungicides added.

Determination of the concentrations of metallic elements in wine also allows calculation of the daily intake of such elements from the wine. Several studies (7) reveal that wine is an important source of iron. The ratio of potassium/sodium in wines is of interest in nutritional studies of the effect of diet on hypertension. Magnesium and aluminum may be toxic to persons with kidney disfunction, which prevents adequate elimination of these elements.

Various techniques have been used to determine several elements in wine, including flame atomic absorption spectrometry (FAAS; 8–10), graphite furnace atomic absorption spectrometry (GFAAS; 11), anodic stripping voltammetry (ASV; 12–14), and inductively coupled plasma-atomic emission spectrometry (ICP-AES; 15).

Atomic absorption-based techniques seem suitable for determining the metallic content of wines. FAAS is especially adequate for metals at relatively high concentration levels. For trace levels, GFAAS is more advisable because of its high sensitivity. Nevertheless, in both FAAS and GFAAS each element is determined individually; this approach involves time-consuming steps in the laboratory.

ASV is a well-established technique for determining trace metals in wines. The principal advantage of ASV is the preconcentration step at the working electrode that leads to extremely low detection limits. However, the presence of organic matter

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may interfere with measurements through absorption on the electrode or formation of organometallic compounds.

ICP-AES has several advantages, compared with atomic absorption techniques: atomization is more complete, plasma is practically free of background radiation, and interferences from ionization or self-absorption are immaterial. Moreover, this technique enables simultaneous determination of all metallic elements. Although detection limits obtained with ICP-AES are higher than those obtained with GFAAS or ASV, they are adequate to quantitate the metals in wine.

The purpose of this study was to apply ICP-AES to the sequential determination of Al, Ca, Cu, Fe, Mg, Mn, Na, K, and Zn in 10 samples of "fino" sherry wines from Jerez, Spain.

Experimental

Apparatus

All glassware and plasticware were washed with deionized water, soaked in 2% HNO_3 overnight, rinsed with deionized water, and air-dried.

(a) *ICP-AES system.*—A sequential plasma Model 40 inductively coupled plasma-atomic emission spectrometer (Perkin-Elmer Corp., Norwalk, CT) attached to an IBM PC-XT computer, and a peristaltic pump for transferring solutions to be measured into the nebulizer.

The instrument was initialized and allowed to achieve thermal equilibrium over 30 min. The instrument had a 40.78 MHz radiofrequency source, 1.1 kW forward power, demountable torch, dual-pass spray chamber (Scott type), and cross-flow nebulizer. Instrumental parameters for analysis were coolant flow, 12 L/min; auxiliary flow, 0.6 L/min (fixed); nebulizer flow, 2.9 L/min; height in plasma, fixed. The sample uptake rate was 1 mL/min. Integration time, which specifies the length of time the instrument measures the emission at each point in a scan, was 300 ms for all elements. The total spectral range around the specified wavelength was 0.50 nm. The background correction interval took into account the distance between the wavelength chosen and the background correction points. The voltage for photomultiplier varied between 400 and 700 V.

(b) *GFAAS system.*—A Perkin-Elmer Model 1100B atomic absorption spectrophotometer, equipped with a Perkin-Elmer HG-500 graphite furnace, a deuterium background corrector, a Model AS-40 automatic injector (Perkin-Elmer), and an Epson FX-800 printer. Aluminum was determined by GFAAS because of the low sensitivity of FAAS. The 309.3 nm wavelength of Al with a spectral bandwidth of 0.7 nm was used. The following temperature program was used for the HG-500 graphite furnace: Dry at 120°C for 25 s; char at 1200°C for 20 s; atomize at 2400°C for 3 s; argon with gas interrupted during atomization.

(c) *FAAS system.*—A Perkin-Elmer Model 2380 atomic absorption spectrophotometer, with the standard nebulization system, an air–acetylene burner, a deuterium background corrector, and an Epson X-400 printer. Operating parameters such as wavelengths, slit widths, and lamp currents were those recommended in the Perkin-Elmer applications manual (16).

(d) *Oven.*—A P-Selecta (Barcelona, Spain) with temperature adjustable from 40° to 200°C (±1.6% homogeneity, ±0.75% stability).

(e) *Graphite tube.*—Pyrocoated graphite plateau tube (No. 94-13053, Perkin-Elmer Corp.).

(f) *Software package for statistical and chemometric procedures.*—CSS.Statistica (Statsoft) statistical package installed on a 486 system.

(g) *Autosampler cups.*—1.5 mL, polystyrene.

(h) *Water purification system.*—Milli-Q (Millipore Corp., Bedford, MA).

Reagents

(a) *Matrix modifier solution.*—Prepared by dissolving 1 g $Mg(NO_3)_2$ analytical reagent (E. Merck, Darmstadt, Germany) in 100 mL deionized water.

(b) *Lanthanum stock solution (5%).*—Prepared by wetting 58.65 g lanthanum(III) oxide for AAS (E. Merck) with deionized water, adding 250 mL concentrated HCl very slowly until material dissolved, and diluting to 1000 mL with deionized water.

(c) *Standard stock solutions of elements.*—1000 μg/mL of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Zn (J.T. Baker, Inc., Berkshire, UK) certified by the manufacturer to ±1% (w/v).

(d) *Working solutions of metals (0.100–30.000 mg/L).*—Prepared by serial dilution of stock solutions with deionized water. The range of concentrations used depended on the elements determined. Working solutions of Ca were prepared with 0.5% lanthanum in 2.5% (v/v) HCl. The pH of the working solutions ranged from 2.5 to 2.7.

Quality control

(a) *Calibration reagent blank.*—Deionized water was used throughout for ICP-AES. The blank was analyzed to establish the baseline after the 10 samples were analyzed (3 integrations for each reading). In those cases where the result was more than 3 standard deviations from the initial value, the instrument was restandardized, and the 10 samples were analyzed again. For FAAS and GFAAS, deionized water or matrix modifier (for determining Al) was used as the blank, with the forementioned criteria.

(b) *Instrument check.*—For daily control of the performance of the ICP-AES and AAS methods, it was advisable to use a reference solution containing the elements of interest. Accordingly, daily analysis of a "control wine" over a long period of time was established. The composition of this wine matrix was as follows: 100 mL ethanol; 7.0 g citric acid; 3.0 g sucrose; 2.0 g glycerol; 3.8 g tartaric acid; 1.5 mL phosphoric acid, and up to 1000 mL water.

This control wine matrix was spiked with known amounts of the elements to be determined by adding certified standard solutions. The final concentrations were midrange values. The resulting solution was the "control wine."

As a daily check on the ICP-AES system before the samples were analyzed, the monochromator was calibrated for the wavelengths selected, and the background emission was corrected. After the analyses, the "control wine" was introduced as

a sample; if the value obtained differed by >10% from the known value, restandardization and reanalysis were required. For analysis by AAS the same criteria were used, with correction of background absorption by the deuterium correction technique.

Procedure

Ten samples of "fino" sherry wines with an alcoholic content of 15.5–16.0% by volume were purchased from commercial stores for analysis.

In each case, 100 mL wine was transferred to a 250 mL beaker and heated in an oven at 80°C for 12 h to remove volatile compounds; approximately 1/5 of the original volume remained after heating. The remaining solution was allowed to cool to room temperature and then was transferred to a 100 mL volumetric flask and diluted to volume with deionized water. The pH of the resulting solution ranged from 2.8 to 3.1, which was very similar to the pH of the standard working solutions. Thus, acidification of the prepared samples before analysis was unnecessary.

The 10 solutions representing the 10 samples were diluted to fall within the most suitable range of concentration for quantitation of the various elements. Thus, the optimal dilutions were 1 to 5 for determination of Al, Cu, Fe, Mn, Na, and Zn and 1 to 25 for determination of K and Mg. Calcium also required 1 to 15 dilution, but 0.5% lanthanum (prepared from stock solution) was used as diluent.

All elements were determined by ICP-AES; the results were compared with those obtained by FAAS (GFAAS for Al) to establish the efficiency of the procedure.

Results and Discussion

Calibration Parameters for ICP Determination

Linearity of the response.—Linearity of the response was evaluated by analyzing standard aqueous solutions ranging in concentration from 0.020 to 4.000 mg/L for the various elements. For Ca, the typical standard curve was obtained with 0.5% lanthanum solutions. The data obtained fit the regression straight line represented by the following equation:

$$I = \text{intercept } (\pm \text{ SD}) + \text{slope } (\pm \text{ SD}) \text{ [concn of element, mg/L], r}$$

where I is intensity of emission and r is the correlation coefficient.

Calibration graphs were linear with correlation coefficients >0.9990 except for Ca (0.9986).

Precision.—Repeatability was evaluated by performing 5 analyses of a wine sample, at the optimal dilution of 1 to 5 or 1 to 25, depending on the elements determined, in 1 day. The relative standard deviations (RSDs) varied from 1.1% (Mg) to 5.3% (Na) (Table 1).

Reproducibility was determined by assaying the same sample of wine in quintuplicate on 3 separate days. The results are shown in Table 1. We found a slight increase in the spread of the results, which did not reach 10%; a spread of up to 15% is acceptable. However, when triplicate determinations were made for real samples, somewhat higher RSD values were found (Table 2). Accordingly, it would be advisable to regard the mean RSD value for each element in Table 2 as a more reliable repeatability parameter.

Table 1. Results from repeatability and reproducibility studies of the determination of metals in "fino" sherry wines

	Repeatability			Reproducibility		
Element	Mean, mg/L[a]	SD, mg/L	RSD, %	Mean, mg/L[a]	SD, mg/L	RSD, %
Al	1.98	0.08	4.14	2.2	0.2	9.30
Ca	97	2	1.84	97	2	2.50
Cu	0.36	0.01	3.61	0.36	0.01	2.77
Fe	4.0	0.2	3.80	4.2	0.2	4.78
K	579	7	1.20	583	10	1.64
Mg	87	1	1.12	89	2	2.03
Mn	0.67	0.01	1.50	0.69	0.02	3.33
Na	46	2	5.33	46	2	5.00
Zn	1.27	0.05	3.90	1.31	0.04	3.43

[a] Each value is the average of 5 replicates.

Sensitivity and detection limit.—The sensitivity of a method is defined as the slope of the calibration curve at the concentration of interest. In the case of calibration straight lines, the sensitivity is the slope of the straight line. In this case (linear response) the sensitivity is highest for Mn, followed by Cu.

The limit of detection (LOD) is defined as the concentration of the element equal to the signal blank plus 3 times the standard deviation (SD) of the blank (17). According to Miller and Miller (18), the SD of regression is equated to the SD of the signal blank, and the intercept is taken as a measure of the signal blank. The limit of quantitation (LOQ) is defined as the lower limit for precise quantitative measurements and is given a value of the signal blank plus 10 times the SD of the blank.

The LOD and LOQ for each element in units of concentration (μg/L) obtained from calibration curves are given in Table 3, which shows that Al is the most easily detected element, followed by Fe, Cu, Mn, and Mg. The LOD for K is very much higher than the LODs for the other elements; however, the expected concentration of this element in "fino" wines presents no quantitation problem.

LODs obtained by ICP-AES are lower than those obtained by FAAS (except the LOD for Al, which is higher by ICP-AES).

Recovery experiments.—The accuracy of the method was measured by determining the recovery of each element from samples fortified prior to any sample preparation procedure. The technique used to determine the absolute recoveries of the different metals consisted of calculating the ratio of the slope of the curve obtained by the method of standard additions to the slope of the conventional calibration curve (19). Recovery data are listed in Table 3. The average recoveries for the individual elements were acceptable, and varied from 97.4% for Cu to 105.7% for Na.

Table 2. Results for determination of metals in 10 sherry wines by ICP-AES

Wine	Al		Ca		Cu	
	Mean ± SD, mg/L[a]	RSD, % (mean RSD)	Mean ± SD, mg/L[a]	RSD, % (mean RSD)	Mean ± SD, mg/L[a]	RSD, % (mean RSD)
1	1.02 ± 0.07	6.9	106 ± 4	3.4	0.07 ± 0.01	13.9
2	1.03 ± 0.08	7.8	107 ± 4	3.4	0.15 ± 0.01	6.7
3	4.1 ± 0.1	3.2	150 ± 6	4.3	0.21 ± 0.02	9.5
4	1.7 ± 0.1	6.4	85 ± 3	3.8	0.52 ± 0.04	7.7
5	2.8 ± 0.2	8.5	96 ± 3	2.7	0.15 ± 0.00	0.00
6	1.2 ± 0.1	8.2	108 ± 2	1.9	0.06 ± 0.01	5.0
7	1.98 ± 0.08	4.1	97 ± 3	2.7	0.63 ± 0.03	4.8
8	1.8 ± 0.2	8.9	87 ± 3	3.8	0.36 ± 0.01	2.8
9	2.57 ± 0.07	2.7	97 ± 2	1.9	1.62 ± 0.03	1.9
10	1.8 ± 0.1	7.8	108 ± 4	3.6	0.38 ± 0.01	2.6
		(6.4)		(3.1)		(5.5)
	Fe		K		Mg	
1	2.3 ± 0.1	4.8	468 ± 9	1.9	83.1 ± 0.7	0.9
2	2.4 ± 0.2	6.2	549 ± 1	2.0	84 ± 1	1.1
3	2.7 ± 0.2	6.4	435 ± 10	2.2	108.6 ± 0.8	0.1
4	3.2 ± 0.4	10.8	614 ± 13	2.1	89 ± 2	1.9
5	2.19 ± 0.08	3.7	514 ± 9	1.7	90.2 ± 0.9	1.0
6	4.9 ± 0.3	6.1	523 ± 19	3.7	76 ± 2	2.2
7	3.9 ± 0.3	8.7	652 ± 4	0.7	84 ± 1	1.2
8	4.0 ± 0.2	3.8	579 ± 7	1.2	87 ± 1	1.1
9	2.72 ± 0.06	2.2	609 ± 15	2.5	94.6 ± 0.3	0.3
10	2.42 ± 0.09	3.7	535 ± 14	2.6	79.1 ± 1.4	1.4
		(5.6)		(2.1)		(1.1)
	Mn		Na		Zn	
1	0.45 ± 0.02	4.4	27.1 ± 0.2	0.5	0.18 ± 0.01	5.6
2	0.59 ± 0.02	3.4	44.75 ± 0.03	0.1	0.25 ± 0.02	8.0
3	2.1 ± 0.1	6.1	48.4 ± 0.7	1.4	0.32 ± 0.03	9.4
4	0.55 ± 0.02	3.2	28.6 ± 0.2	0.7	5.1 ± 0.2	4.3
5	0.37 ± 0.01	2.7	42.2 ± 0.4	1.0	0.12 ± 0.01	8.3
6	0.60 ± 0.04	6.7	27.3 ± 0.8	3.1	0.53 ± 0.06	11.3
7	0.70 ± 0.04	5.7	46 ± 2	5.3	1.3 ± 0.1	7.9
8	0.67 ± 0.01	1.5	39.9 ± 0.8	1.9	1.27 ± 0.05	3.9
9	0.76 ± 0.02	2.6	54.3 ± 0.7	1.3	1.13 ± 0.05	4.4
10	0.61 ± 0.02	3.3	35 ± 1	2.8	0.37 ± 0.05	13.5
		(3.9)		(1.8)		(7.6)

[a] Each value is the average of 3 replicates.

Application to wine samples.—Results obtained by ICP-AES for analysis of 10 wine samples are shown in Table 2. In all cases the concentrations of the various elements are very much higher than the previously established LODs.

Certain observations can be made about the values shown in Table 2. In general, the results are in agreement with the literature values (20) for this type of wine.

The concentration of Al falls between 1.02 and 2.83 mg/L, except in sample 3, where it exceeds 4 mg/L. The precision of the analytical procedure is considered acceptable for Al, with RSD values ranging from 2 to 9%.

Copper concentrations range from 0.06 to 1.62 mg/L; the percent difference between the mean and the highest value in the concentration range is greater for Cu than for any other element in the samples analyzed. Although the Cu concentrations are low, the RSD values for all the samples except sample 1 are <10%.

Iron concentrations are high compared with the concentrations of Al and Cu and range from 2.3 to 4.9 mg/L; in no case is the RSD for Fe >10.8%.

Data for Mn show that the precision of the ICP-AES technique is very high for this element; RSD values are <7% for all

Table 3. Wavelengths, detection and quantitation limits, and mean recoveries for elements determined by ICP-AES

Element	Wavelength, nm (Linear range, mg/L)	LOD, μg/L	LOQ, μg/L	Spiking level, mg/L (Recovery, %)	Mean recovery, %
Al	237.335 (0.02–2.00)	15.2	50.0	0.2, 0.5, 1.0 (104.2) (104.8) (95.7)	101.6
Ca	393.366 (0.20–4.00)	39.9	133.0	20.0, 50.0, 70.0 (103.3) (105.2) (102.2)	103.6
Cu	324.754 (0.02–2.00)	20.1	67.0	0.1, 0.3, 0.5 (101.7) (95.6) (95.0)	97.4
Fe	239.562 (0.20–4.00)	19.1	63.7	0.6, 2.0, 3.0 (101.0) (100.3) (99.6)	100.3
K	766.490 (2.00–30.00)	116.4	388.0	100.0, 200.0, 300.0 (100.8) (101.8) (100.4)	100.7
Mg	279.553 (0.20–4.00)	20.3	67.7	15.0, 25.0, 40.0 (101.1) (104.5) (105.3)	103.6
Mn	257.610 (0.02–2.00)	20.2	67.3	0.2, 0.5, 1.0 (101.4) (97.5) (98.4)	99.1
Na	589.592 (1.00–10.00)	34.6	115.3	10.0, 20.0, 30.0 (101.8) (107.1) (108.1)	105.7
Zn	202.548 (0.02–2.00)	25.4	84.7	0.2, 0.5, 1.0 (102.8) (105.2) (91.7)	99.9

samples. These results are evidence of the good relationship between the signals of the element and the baseline (background), which is of the order of 0.01 mg/mL. Manganese levels are similar to Cu levels, and are fairly consistent in all samples (0.45–0.76 mg/L), except sample 3, which contains 2.1 mg/L.

Sodium, usually the element found at a high level in any type of sample, is no exception in "fino" wines, which contain >25 mg/L in all cases. The precision of the results is excellent; all RSD values are <3%, except those for samples 6 and 7, which are 3.1 and 5.3%, respectively.

Zinc concentrations are between 0.12 and 1.27 mg/L except for a very high value of 5.1 mg/L found in sample 4. The RSD values are <14%.

All elements were quantitated from 1 to 5 dilutions of the wines. Samples which have an exceptionally high content of any of the elements, or RSDs that are >10%, vary at random.

Data for Ca, K, and Mg, which were measured from 1 to 25 dilutions of the wines, complete Table 2. The overall range for Ca in sherry wines is 85–150 mg/L. RSDs are <5% for all samples analyzed. Potassium and magnesium are present at even higher concentrations than the rest of the elements, i.e., about 70–600 mg/L; consequently, the precision is excellent, and most RSD values are <2%.

Method Validation

To validate the new proposed method, concentrations were simultaneously measured by using another reputable or standard procedure, FAAS (GFAAS for Al). The results of the comparative study of elements determined by ICP-AES and AAS are shown in Table 4. AAS values for the metals Al, K, and Mg are higher than those obtained by ICP-AES, whereas Cu, Ca, Fe, Mn, Na, and Zn values are very similar in both cases, being arbitrarily higher or lower in the different samples by one method or the other. RSD values for the different metals quantitated by AAS range from 3.1 to 12.8%.

Although there are different ways of comparing analytical results obtained by 2 techniques, we chose the method of regression lines (18) obtained from points corresponding to the concentrations found in each sample analyzed by the 2 procedures. The method is acceptable and reliable, because it can be applied to a wide and variable range of analyte concentrations.

The y-axis of a regression graph was used for the results obtained by ICP-AES, and the x-axis was used for the results obtained by AAS.

If errors were absent, a theoretical slope of 1 and an intercept of 0 would be expected. Taking into account the occurrence of random errors, we applied a significance test for both slope and intercept obtained from each regression. According to the Student's *t*-test (at a 5% level of significance) there are nonsignificant differences between the results obtained by both methods.

Therefore, it may be concluded that the ICP-AES and FAAS or GFAAS (Al) methods do not give significantly different results for any of the elements assayed.

Another way to validate a method is to perform the calibration by the method of standard additions (21) to detect and correct possible effects of the matrix. Three standard addition samples of the wines, spiked with adequate known quantities of each element, were prepared in quintuplicate and measured by ICP-AES. The mean values for each element are shown in Table 5, together with those obtained by direct calibration, also measured in quintuplicate.

The results by both methods were similar. Comparison of the mean values by the Student's *t*-test (22) did not reveal significant differences at the 95% confidence level. Therefore, it is not necessary to use the method of standard additions in the

Table 4. Results for determination of elements (mg/L) in "fino" sherry wines by ICP–AES and AAS[a]

Sample	ICP-AES	GFAAS	ICP-AES	FAAS	ICP-AES	FAAS
	Al		Ca		Cu	
1	1.02	1.49	106	110	0.07	0.11
2	1.03	1.58	107	105	0.15	0.19
3	4.1	4.8	150	149	0.21	0.24
4	1.7	2.6	85	89	0.52	0.51
5	2.8	3.7	96	95	0.15	0.17
6	1.2	1.9	108	111	0.06	0.08
7	1.98	2.91	97	95	0.63	0.68
8	1.8	2.7	87	94	0.36	0.39
9	2.57	3.54	97	102	1.62	1.64
10	1.8	2.7	108	106	0.38	0.41
	Fe		K		Mg	
1	2.3	2.4	468	475	83.1	93.75
2	2.4	2.5	549	577	84	94.45
3	2.7	2.7	435	438	108.57	116.75
4	3.2	3.1	614	586	88.73	100.35
5	2.19	2.34	514	512	90.22	103.71
6	4.9	4.8	523	503	76.27	88.80
7	3.9	4.0	652	614	84.13	95.51
8	4.0	3.9	579	573	87.32	95.11
9	2.72	2.78	609	605	94.57	104.90
10	2.42	2.47	535	558	79.40	92.40
	Mn		Na		Zn	
1	0.45	0.40	27.09	28.91	0.18	0.17
2	0.59	0.54	44.75	38.00	0.25	0.26
3	2.13	2.05	48.41	43.46	0.32	0.34
4	0.55	0.42	28.61	28.91	5.24	5.30
5	0.37	0.28	42.21	39.21	0.12	0.15
6	0.60	0.54	27.31	27.09	0.53	0.56
7	0.70	0.58	45.58	42.55	1.26	1.35
8	0.67	0.54	39.94	38.61	1.27	1.33
9	0.76	0.65	54.26	46.49	1.13	1.19
10	0.61	0.47	34.95	35.88	0.37	0.43

[a] Each value is the average of 3 replicates.

proposed simultaneous assay of the elements; thus, less time and work are needed for its completion.

Conclusions

A simple and rapid method was evaluated for the sequential assay of 9 elements in "fino" wine samples by ICP-AES. The wine sample is simply heated in an oven, to eliminate the ethanol, and diluted 1 to 5 or 1 to 25 with ultrapure water, depending on the elements determined.

It is not necessary to apply the method of standard additions to determine any of the elements. Estimated limits of detection and quantitation were lower than the concentrations found for each element. The mean recoveries of all elements ranged from 97.4 to 105.7%. The repeatability and reproducibility RSDs were <10%.

The results obtained by ICP-AES are not significantly different from those obtained by AAS techniques (FAAS and GFAAS).

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Table 5. Concentrations of several elements determined in wines by linear calibration and method of standard additions

Element	Linear calibration		Standard additions		Student's *t*-test, p level
	Mean[a]	S_{n-1}	Mean[a]	S_{n-1}	
Al	1.98	0.04	1.93	0.28	0.73
Ca	98.30	1.86	99.20	3.50	0.61
Cu	0.36	0.01	0.36	0.04	0.99
Fe	3.95	0.14	4.27	0.28	0.05
K	540.84	33.09	559.40	52.56	0.52
Mg	83.59	1.91	80.83	3.29	0.14
Mn	0.67	0.01	0.63	0.09	0.32
Na	45.59	2.43	48.96	4.48	0.18
Zn	1.27	0.05	1.38	0.09	0.05

[a] Each value is the average of 5 replicates.

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