Searching the Most Appropriate Sample Pretreatment for the Elemental Analysis of Wines by Inductively Coupled Plasma-Based Techniques

A. Gonzálvez, S. Armenta, A. Pastor, and M. de la Guardia*

Department of Analytical Chemistry, Research Building, University of Valencia, 50th Dr. Moliner St.,
E-46100 Burjassot, Valencia, Spain

Different sample preparation methods were evaluated for the simultaneous multielement analysis of wine samples by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Microwave-assisted digestion in closed vessel, thermal digestion in open reactor, and direct sample dilution were considered for the determination of Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Y, Mo, Cd, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, and Bi in 12 samples of red wine from Valencia and Utiel-Requena protected designation of origin. ICP-MS allows the determination of 17 elements in most of the samples, and using ICP-OES, a maximum of 15 elements were determined. On comparing the sample pretreatment methodology, it can be concluded that the three assayed procedures provide comparable results for the concentration of Li, Na, Mg, Al, K, Ca, Mn, Fe, Zn, and Sr by ICP-OES. Furthermore, ICP-MS data found for Cu, Pb, and Ba were comparable. Digestion treatment provides comparable values using both total decomposition in open system and microwave-assisted treatment for Cu by ICP-OES and for Cr, Ni, and Zn by ICP-MS. Open vessel total digestion provides excess values for Cr, Mn, Fe, and Zn by ICP-OES and defect values for Se. However, direct measurement of diluted wine samples provided uncomparable results with the digestion treatment for Mn, Cu, Pb, Zn, Ba, and Bi by ICP-OES and for Mg, Cr, Fe, Ni, and Zn by ICP-MS. Therefore, it can be concluded that microwave-assisted digestion is the pretreatment procedure of choice for elemental analysis of wine by ICP-based techniques.

KEYWORDS: Wine; ICP-OES; ICP-MS; multielemental analysis; sample pretreatment

INTRODUCTION

The determination of the elemental composition of wines is of great interest for the characterization of samples and also for the identification of wine origin (*1–4*). To do it in an appropriate way, there is no single element to be determined, but it is necessary to accurately determine, as much as possible minor, trace and ultra trace elements.

Different techniques such as flame atomic absorption spectroscopy (FAAS) (*5*), graphite furnace atomic absorption spectroscopy (GFAAS) (*6*), and voltammetry (*7*) have been employed for the determination of metals in wines. However, the most extensively employed techniques to do the elemental characterization of wines are inductively coupled plasma mass spectrometry (ICP-MS) (*8–10*) and inductively coupled plasma optical emission spectrometry (ICP-OES) (*11–13*), which are suitable for the simultaneous or fast sequential determination of trace and ultratrace elements. Those techniques provide a multielement detection capability and a wide linear dynamic range (4−6 orders of magnitude), which permits the determination of several elements in a same sample.

Wine, from an analytical point of view, is a complex matrix with water and ethanol as the main components containing Fe, K, Mg, Ca, Na, and Al at the ppm level and around 15 elements that are commonly present at the ppb level. Additionally, there are hundreds of organic compounds present in wines, which can cause spectral and nonspectral interferences. Therefore, it is clear that sample pretreatment as well as the method of determination is critical for the accuracy of the determination of trace and ultratrace elements, as has been probed previously (*14*).

The selection of a sample preparation procedure implies that one must obtain the best results in the shortest time, with minimum loses or contamination risks, using the smallest quantities of reagents and samples, and generating little amounts of residues and wastes. Thus, different sample pretreatments have been described in the literature for the determination of metal content in wines by ICP-MS and ICP-OES, such as microwave-assisted acid digestion (*8, 11, 24*), thermal digestion in open reactor (*15, 16*), sample dilution (*17–20*), or dry ashing (*21*).

* Corresponding author. Tel. +34-963544838. Fax: + 34-963544838. E-mail: miguel.delaguardia@uv.es.

Table 1. Operating Conditions for Multielemental Analysis of Wine Using ICP-OES and ICP-MS

ICP-OES	
parameters	value
radio frequency power	1400 W
gas	argon
plasma gas	15 L min^{-1}
auxiliary gas	0.2 L min^{-1}
nebulizer gas	0.8 L min^{-1}
sample aspiration rate	1.1 mL min^{-1}
view	axial
background correction	2-point
number of replicates	1
nebulizer	Meinhard
ICP-MS	
radio frequency power	1125 W
gas	argon
plasma gas	15 L min^{-1}
auxiliary gas	1.2 L min^{-1}
nebulizer gas	0.95 L min^{-1}
lens voltage	6.5 V
detector	dual
dwell time	50 ms
sweeps/readings	6
replicate/readings	1
replicates	2
nebulizer	Meinhard

The aim of this study has been to do a critical evaluation of sample pretreatments commonly employed for the determination of trace elements in wines by inductively coupled plasma-based techniques. Accuracy has been the main criterion for selecting the best sample treatment. In our study, accuracy has been evaluated by the comparison of results found by ICP-OES and ICP-MS for 12 different samples after being treated by two digestion procedures and just dilution.

EXPERIMENTAL PROCEDURES

Reagents and Apparatus. Stock solutions of a multielemental standard solution (100 μg mL^{-1}) containing 26 elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Na, Sr, Tl, Ti, V, and Zn) dissolved in 5% HNO$_3$ from Scharlau (Barcelona, Spain) and a multielemental (100 μg mL^{-1}) solution containing 16 lanthanides dissolved in 5% HNO$_3$ from Alfa Aesar (Karlsruhe, Germany) were employed for calibration.

HNO$_3$ 69% (w/v) from J.T. Baker (Deventer, The Netherlands), H$_2$O$_2$ 35% (v/v) reagent grade from Scharlau, perchloric acid 60% (w/v) from Panreac (Barcelona, Spain), absolute ethanol from Scharlau, and nanopure water with a maximum resistivity of 18.2 MΩ cm^{-1} obtained from a Milli-Q Millipore system (Bedford, MA, USA) were used for sample treatment and sample dilution.

A microwave laboratory system Ethos SEL from Millestone (Sorisole, Italy), equipped with an optical fiber sensor for automatic temperature control, an automatic gas detector and operating at a maximum exit power of 1000 W, was employed for microwave-assisted digestion of wine samples introduced inside 10 high pressure vessels of 100 mL inner volume.

An ultrasound water bath from Selecta (Barcelona, Spain) of 350 mL volume, with 50 W power and 50 Hz frequency, was employed for sample sonication.

Measurements by ICP-OES were carried out using a PerkinElmer Model Optima 5300 DV spectrometer (Norwalk, CT, USA) equipped with an autosampler AS 93-plus and a Meinhard nebulizer. Argon C-45 (purity higher than 99.995%), supplied by Carburos Metálicos (Barcelona, Spain), was employed as plasmogen and carrier gas.

ICP-MS measurements were carried out with a Perkin-Elmer SCIEX Elan 6100 DRCII apparatus (Norwalk, CT, USA), equipped with a Meinhard nebulizer. An autosampler Perkin-Elmer AS-91 was used for sample introduction in both measurement systems.

Samples. Twelve red Spanish wine samples were employed in this study. Samples were categorized into three classes as a function of their origin (P.D.O.), three samples from Utiel Requena P.D.O., three from Valencia P.D.O. and six from Fontanars dels Alforins, the last ones also corresponding to the Valencia P.D.O. Wine bottles were purchased in liquor retail stores and markets. The alcoholic content ranged from 12 to 14.2% v/v ethanol, and their vintages in all cases were between 2001 and 2005.

The plastic containers used for storing and diluting the samples were cleaned to avoid contamination by trace metals. Containers were treated with nitric acid and washed with milli-Q water before washing with the samples. Once opened, the wine samples were treated according to the three evaluated pretreatment procedures.

Table 2. Analytical Features of ICP-OES and Semi-Quantitative ICP-MS for the Determination of Trace Elements in Wines after Dilution or Digestion of Samples[a]

	ICP-MS				ICP-OES			
	dilution		digestion		dilution		digestion	
	LOD[b] (μg L^{-1})	% RSD	LOD[b] (μg L^{-1})	% RSD	LOD[c] (μg L^{-1})	% RSD	LOD[c] (μg L^{-1})	% RSD
Li	0.016	7	7.5×10^{-6}	5	0.11	0.4	0.07	0.1
Na			2.9×10^{-6}	6	0.3	0.3	0.12	0.5
Mg		3	8.9×10^{-5}	4	0.06	0.6	0.10	1.9
Al	20	10	2.9×10^{-5}	17	0.8	7	0.08	3
K			0.2	3	0.2	0.9	0.12	1.2
Ca			0.5		0.16	1.6	0.13	1.9
Sc	0.07	4	0.5	8	0.02	1	0.05	0.2
Ti	0.16	10	0.5		0.06	2	0.09	0.9
V	0.12	5	0.25	5	0.08	0.7	0.05	0.3
Cr	15	8	0.5		0.4	0.9	0.11	0.5
Mn	0.7	4	3.7×10^{-6}	6	0.03	0.7	0.03	0.3
Fe		9	4.1×10^{-4}		0.03	20.0	0.07	2
Ni	3	7	1.5×10^{-6}		2	8	0.1	2
Cu	0.8	11	0.05		0.19	1.6	0.4	0.5
Zn	2	8	7.9×10^{-6}	5	0.2	3	0.07	0.5
Se		11			1	3	6	20
Sr	0.03	2	1.9×10^{-6}	2	0.05	0.9	0.03	0.9
Ba	0.6	7	5.1×10^{-7}	3	0.09	0.4	0.02	0.5
Pb	0.12	5	0.05	4	2	25	11	20
Bi	0.06	3	1.7×10^{-6}	2	1.9	3	4	5.7

[a] Se was not determined by ICP-MS, and for mayor elements, the LOD values in ICP-MS have no sense because we did not found any sample undetectable contents.
[b] LOD values were calculated as the concentrations corresponding to signals equal to three-times the standard deviation of a 0.5 μg L^{-1} solution signal (three replicates).
[c] LOD values were calculated as the concentrations corresponding to signals equal to three-times the standard deviation of a blank solution signal (three replicates).
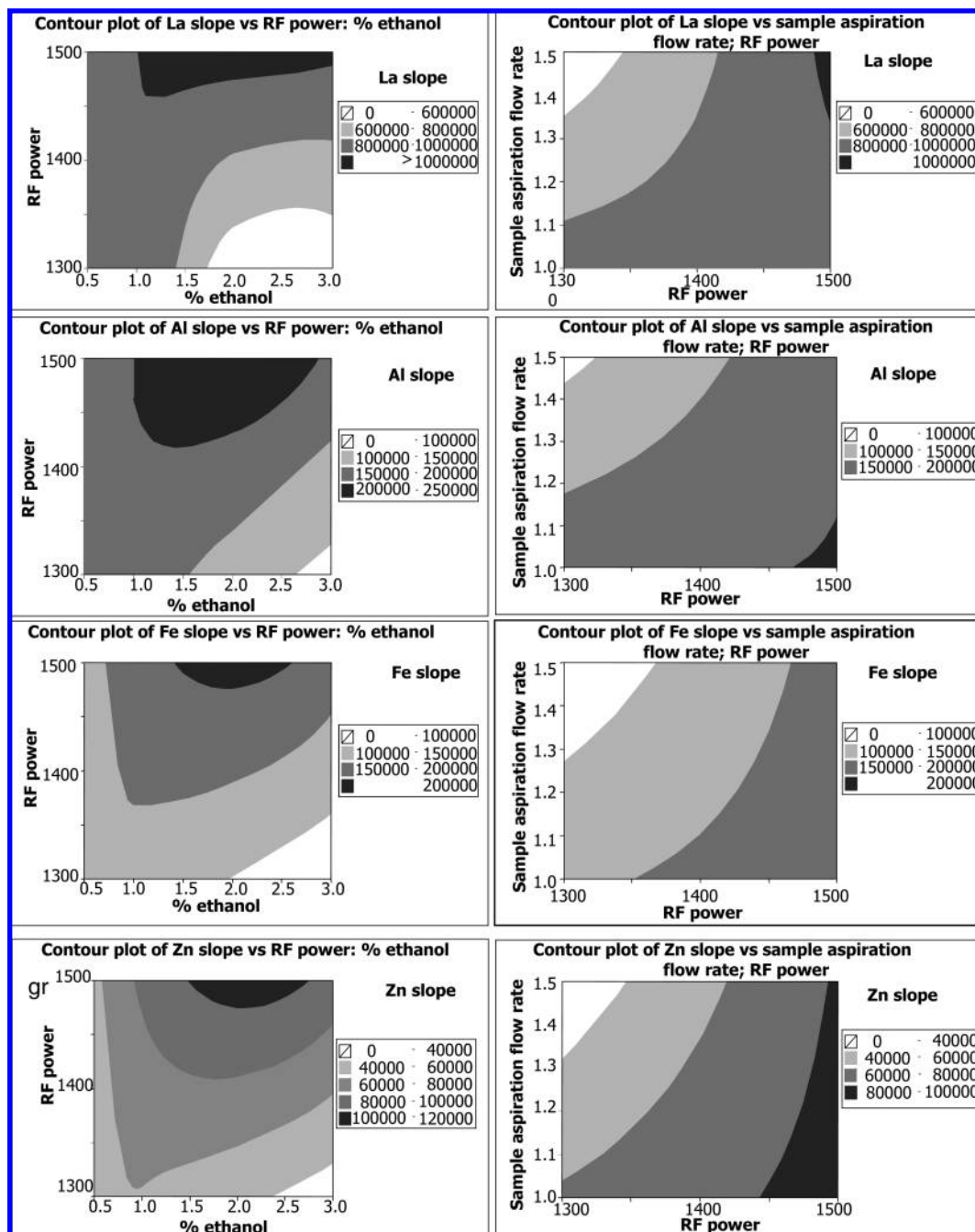
Elemental Analysis of Wines

J. Agric. Food Chem., Vol. 56, No. 13, 2008 **4945**

Figure 1. Contour plots of the effect of radio frequency power (RF), sample aspiration flow rate, and sample dilution factor on the sensitivity of La, Al, Fe, and Zn determination by ICP-OES.

Sample Pretreatment. The most common preparation methods used for wine analysis are wet acid digestion and dilution. Wet digestion is made for partial or total decomposition of the organic matter and can be performed in closed or open vessels, using convective thermal energy or microwave radiation. Alternatively, direct analysis of wine samples diluted with water seems to be a fast and precise way for sample preparation.

Microwave-Assisted Digestion. The microwave-assisted treatment was adapted from that of Galani-Nikolakaki et al. (*22*) according to the microwave laboratory system manufacturer's recommendations. Teflon digestion vessels were previously cleaned in nitric solution to avoid cross-contamination. Two milliliters of red wine were weighted inside the digestion vessels, and 8 mL of concentrated nitric acid was added. Once the vessel was capped, it was placed in the microwave oven, and the following program was run: 3 min to reach 85 °C; 12 min to reach 145 °C; 6 min to reach 180 °C; 15 min at 180 °C; and a final cool down. After cooling to ambient temperature, reactors were

opened and sonicated to eliminate nitrous vapors. The resultant solution was transferred inside a plastic flask and diluted to a final volume of 25 mL.

Open Vessel Total Digestion. Acid digestion of wine samples in open vessels was based on the method reported by Lara et al. (*23*). One milliliter of concentrated perchloric acid and 2 mL of concentrated nitric acid were added to 5 mL of wine, and the sample was digested by heating the mixture until dryness in a pyrex glass of 50 mL volume. To avoid external and cross-contamination of samples, single-use plastic Pasteur pipettes were used to transfer samples and reagents. The white ashes obtained by this procedure were dissolved in 0.5 mL of concentrated nitric acid, and the solution was diluted with milli-Q water to a final volume of 25 mL.

Dilution. A 10-times dilution of wine samples, without any further sample preparation, was also checked as sample pretreatment. In this sense, 1 mL of sample was introduced in a plastic flask, and 75 μL of concentrated

Table 3. Data of the Elemental Composition of Wines Obtained by ICP-OES after Different Sample Pretreatments[a]

| | D.O. Valencia 1 | | | D.O. Valencia 2 | | | D.O. Valencia 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.1014 ± 0.0001	0.1161 ± 0.0001	0.1055 ± 0.0004	0.1195 ± 0.0001	0.1242 ± 0.0001	0.1127 ± 0.0004	0.09032 ± 0.00009	0.1332 ± 0.0001	0.0986 ± 0.0004
Na	42.4 ± 0.2	45.8 ± 0.2	46.08 ± 0.1	31.8 ± 0.1	29.4 ± 0.1	30.36 ± 0.09	26.9 ± 0.1	25.2 ± 0.1	27.12 ± 0.08
Mg	81 ± 1	82 ± 1	82.3 ± 0.5	84 ± 1	90 ± 1	87.9 ± 0.5	84 ± 1	83 ± 1	82.0 ± 0.5
Al	1.01 ± 0.03	0.94 ± 0.03	0.950 ± 0.06	1.23 ± 0.03	1.08 ± 0.03	1.20 ± 0.08	1.04 ± 0.03	1.03 ± 0.03	1.00 ± 0.08
K	1003 ± 12	1002 ± 12	1095 ± 10	961 ± 11	845 ± 10	923 ± 8	1009 ± 12	914 ± 11	922 ± 8
Ca	55 ± 1	55 ± 1	56.0 ± 0.8	45.1 ± 0.8	43.3 ± 0.8	45.8 ± 0.7	44.7 ± 0.8	42.4 ± 0.8	42.2 ± 0.6
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	0.672 ± 0.002	0.688 ± 0.002	0.659 ± 0.004	0.731 ± 0.002	0.710 ± 0.002	0.712 ± 0.004	0.925 ± 0.002	0.989 ± 0.002	0.946 ± 0.006
Fe	2.93 ± 0.06	2.70 ± 0.05	2.6 ± 0.5	1.71 ± 0.03	1.46 ± 0.03	1.3 ± 0.3	1.63 ± 0.03	1.24 ± 0.02	1.5 ± 0.3
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zn	0.242 ± 0.001	0.223 ± 0.001	0.218 ± 0.006	0.1822 ± 0.0009	0.1864 ± 0.0009	0.208 ± 0.006	0.267 ± 0.001	0.282 ± 0.001	0.243 ± 0.006
Se	<LOD	0.83 ± 0.1	0.83 ± 0.02	<LOD	0.82 ± 0.1	<LOD	<LOD	0.44 ± 0.08	0.41 ± 0.01
Sr	0.588 ± 0.005	0.598 ± 0.005	0.574 ± 0.005	0.717 ± 0.006	0.701 ± 0.006	0.703 ± 0.006	0.809 ± 0.007	0.849 ± 0.007	0.803 ± 0.007
Ba	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	0.25 ± 0.06	<LOD	<LOD	0.14 ± 0.03	<LOD	<LOD	<LOD
Bi	<LOD	<LOD	0.187 ± 0.005	<LOD	<LOD	0.177 ± 0.005	<LOD	<LOD	<LOD

| | D.O. Utiel Requena 1 | | | D.O. Utiel Requena 2 | | | D.O. Utiel Requena 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.1172 ± 0.0001	0.1363 ± 0.0001	0.12001 ± 0.0004	0.1152 ± 0.0001	0.1116 ± 0.0001	0.1165 ± 0.0004	0.1314 ± 0.0001	0.1314 ± 0.0001	0.1337 ± 0.0004
Na	31.7 ± 0.1	31.8 ± 0.1	31.33 ± 0.1	39.4 ± 0.1	30.2 ± 0.1	35.86 ± 0.1	18.2 ± 0.09	17.3 ± 0.09	18.75 ± 0.05
Mg	82 ± 1	99 ± 1	94.2 ± 0.5	93 ± 1	96 ± 1	98.5 ± 0.6	71 ± 1	73 ± 1	70.8 ± 0.4
Al	1.00 ± 0.03	1.22 ± 0.03	1.00 ± 0.07	1.02 ± 0.03	1.40 ± 0.03	1.06 ± 0.07	1.22 ± 0.03	1.10 ± 0.03	1.08 ± 0.07
K	1062 ± 12	1072 ± 12	1150 ± 9	1122 ± 12	1099 ± 12	1020 ± 9	691 ± 8	642 ± 8	689 ± 6
Ca	45.5 ± 0.8	44.4 ± 0.8	46.7 ± 0.7	46.4 ± 0.8	45.8 ± 0.8	48.8 ± 0.7	60 ± 1	62 ± 1	63 ± 1
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	0.12 ± 0.06	0.14 ± 0.06	<LOD	0.12 ± 0.06	0.14 ± 0.06	<LOD	0.12 ± 0.06	0.13 ± 0.06	<LOD
Mn	0.661 ± 0.002	0.722 ± 0.002	0.658 ± 0.005	0.667 ± 0.002	0.691 ± 0.002	0.673 ± 0.005	0.588 ± 0.002	0.620 ± 0.002	0.597 ± 0.005
Fe	2.09 ± 0.04	2.25 ± 0.04	2.1 ± 0.4	2.59 ± 0.04	2.63 ± 0.04	2.4 ± 0.4	2.07 ± 0.04	1.98 ± 0.04	2.0 ± 0.4
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	0.414 ± 0.002	0.505 ± 0.002	<LOD	0.322 ± 0.001	0.359 ± 0.001	<LOD	<LOD	<LOD	<LOD
Zn	0.262 ± 0.001	0.217 ± 0.001	0.232 ± 0.007	0.262 ± 0.001	0.246 ± 0.001	0.257 ± 0.007	0.269 ± 0.001	0.221 ± 0.001	0.252 ± 0.007
Se	0.8 ± 0.1	0.8 ± 0.1	0.78 ± 0.02	0.09 ± 0.02	1.1 ± 0.2	0.83 ± 0.02	<LOD	0.33 ± 0.06	1.02 ± 0.03
Sr	0.997 ± 0.009	1.103 ± 0.009	0.983 ± 0.009	1.055 ± 0.009	1.072 ± 0.009	1.045 ± 0.009	1.25 ± 0.01	1.26 ± 0.01	1.22 ± 0.01
Ba	0.1002 ± 0.0005	0.1172 ± 0.0005	<LOD	0.1111 ± 0.0005	0.1154 ± 0.0005	0.1126 ± 0.0004	0.1033 ± 0.0005	0.0952 ± 0.0005	<LOD
Pb	<LOD	<LOD	0.19 ± 0.05	<LOD	<LOD	0.22 ± 0.05	<LOD	<LOD	0.25 ± 0.05
Bi	<LOD	<LOD	0.183 ± 0.005	<LOD	<LOD	0.179 ± 0.005	<LOD	<LOD	<LOD

| | Fontanars dels Alforins 1 | | | Fontanars dels Alforins 2 | | | Fontanars dels Alforins 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.1283 ± 0.0001	0.1934 ± 0.0001	0.2256 ± 0.0004	0.2442 ± 0.0001	0.2176 ± 0.0001	0.2191 ± 0.0004	0.2501 ± 0.0001	0.2284 ± 0.0001	0.2552 ± 0.0004
Na	29.1 ± 0.1	26.4 ± 0.1	28.01 ± 0.08	37.1 ± 0.1	34.5 ± 0.1	36.70 ± 0.1	25.6 ± 0.1	22.4 ± 0.1	23.43 ± 0.07
Mg	144 ± 2	137 ± 2	146.5 ± 0.8	155 ± 2	151 ± 2	158.0 ± 0.8	174 ± 2	174 ± 2	175.8 ± 0.8
Al	2.51 ± 0.07	2.34 ± 0.07	2.5 ± 0.2	2.19 ± 0.07	2.42 ± 0.07	2.5 ± 0.2	2.67 ± 0.07	2.57 ± 0.07	2.5 ± 0.2
K	1048 ± 12	987 ± 12	1019 ± 9	1088 ± 12	993 ± 12	1051 ± 9	904 ± 12	835 ± 11	845 ± 7
Ca	53 ± 1	53 ± 1	53.6 ± 0.8	50 ± 1	55 ± 1	54.4 ± 0.8	76 ± 1	84 ± 1	79.5 ± 1
Sc	0.1003 ± 0.0002	0.1086 ± 0.0002	<LOD	0.0961 ± 0.0002	0.1094 ± 0.0002	<LOD	0.0832 ± 0.0002	0.0723 ± 0.0002	<LOD
Ti	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	0.0593 ± 0.0003	0.0531 ± 0.0003	<LOD	0.301 ± 0.001	0.430 ± 0.001	<LOD	1.796 ± 0.009	0.0572 ± 0.0003	<LOD
Mn	1.163 ± 0.003	0.0572 ± 0.0002	1.110 ± 0.007	0.626 ± 0.002	0.517 ± 0.002	1.270 ± 0.007	1.150 ± 0.003	0.527 ± 0.002	1.451 ± 0.007
Fe	2.43 ± 0.05	2.19 ± 0.05	2.8 ± 0.6	3.57 ± 0.05	3.07 ± 0.05	3.1 ± 0.6	9.7 ± 0.2	2.16 ± 0.05	2.2 ± 0.5
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	0.318 ± 0.001	0.188 ± 0.001	0.179 ± 0.003	<LOD	<LOD	<LOD	0.172 ± 0.001	0.052 ± 0.001	0.0435 ± 0.0002
Zn	0.743 ± 0.004	<LOD	0.73 ± 0.02	0.1626 ± 0.0008	<LOD	0.232 ± 0.007	0.672 ± 0.004	0.0992 ± 0.0005	0.65 ± 0.02
Se	0.08 ± 0.02	0.5 ± 0.1	0.55 ± 0.02	0.07 ± 0.02	0.5 ± 0.1	0.57 ± 0.02	0.04 ± 0.02	0.6 ± 0.1	0.58 ± 0.02
Sr	0.844 ± 0.007	0.878 ± 0.007	0.811 ± 0.007	1.16 ± 0.01	1.17 ± 0.01	1.09 ± 0.01	2.50 ± 0.02	2.25 ± 0.02	2.11 ± 0.02
Ba	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bi	0.28 ± 0.02	0.20 ± 0.02	0.211 ± 0.006	0.13 ± 0.01	0.09 ± 0.01	0.111 ± 0.006	0.08 ± 0.01	0.06 ± 0.01	0.690 ± 0.02

Elemental Analysis of Wines

J. Agric. Food Chem., Vol. 56, No. 13, 2008 **4947**

Table 3. Continued

	Fontanars dels Alforins 4			Fontanars dels Alforins 5			Fontanars dels Alforins 6		
	acid digestion			acid digestion			acid digestion		
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.2195 ± 0.0002	0.2051 ± 0.0002	0.2424 ± 0.0009	0.1667 ± 0.0002	0.1943 ± 0.0002	0.2886 ± 0.0009	0.1966 ± 0.0002	0.1963 ± 0.0002	0.2022 ± 0.0009
Na	30.9 ± 0.1	35.3 ± 0.1	33.5 ± 0.1	25.1 ± 0.1	28.1 ± 0.1	27.3 ± 0.1	17.44 ± 0.08	12.92 ± 0.08	15.37 ± 0.06
Mg	154 ± 3	147 ± 3	154.2 ± 0.8	127 ± 2	127 ± 2	130.0 ± 0.8	141 ± 3	132 ± 3	137.1 ± 0.8
Al	2.54 ± 0.07	2.44 ± 0.07	2.5 ± 0.2	2.28 ± 0.07	2.04 ± 0.07	2.5 ± 0.2	2.12 ± 0.07	2.30 ± 0.07	2.4 ± 0.2
K	1322 ± 19	1181 ± 14	1341 ± 12	686 ± 8	613 ± 8	683 ± 6	1103 ± 13	936 ± 9	1054 ± 9
Ca	61 ± 1	66 ± 1	64.2 ± 0.9	70 ± 1	72 ± 1	71 ± 1	61 ± 1	63 ± 1	61.9 ± 0.9
Sc	0.04317 ± 0.00008	0.1071 ± 0.0002	<LOD	0.04753 ± 0.00008	0.1085 ± 0.0002	<LOD	0.04423 ± 0.00008	0.1018 ± 0.0002	<LOD
Ti	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	0.0325 ± 0.0002	0.0502 ± 0.0002	<LOD	0.0613 ± 0.0002	0.0550 ± 0.0002	<LOD	0.0466 ± 0.0002	0.0401 ± 0.0002	<LOD
Mn	0.739 ± 0.002	0.185 ± 0.001	1.200 ± 0.008	0.787 ± 0.002	0.532 ± 0.001	1.510 ± 0.008	1.609 ± 0.005	1.095 ± 0.005	1.607 ± 0.008
Fe	3.491 ± 0.007	3.345 ± 0.007	3.9 ± 0.4	2.203 ± 0.006	2.103 ± 0.006	2.2 ± 0.4	2.000 ± 0.006	1.902 ± 0.006	1.9 ± 0.4
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zn	0.0763 ± 0.0004	<LOD	0.44 ± 0.01	<LOD	<LOD	0.33 ± 0.01	9.46 ± 0.05	8.83 ± 0.05	9.4 ± 0.3
Se	0.07 ± 0.01	0.57 ± 0.1	0.61 ± 0.02	0.09 ± 0.01	0.33 ± 0.06	0.58 ± 0.01	0.018 ± 0.003	0.5 ± 0.1	0.46 ± 0.01
Sr	1.093 ± 0.009	1.034 ± 0.009	1.081 ± 0.009	0.839 ± 0.007	1.009 ± 0.009	0.788 ± 0.007	1.209 ± 0.009	1.191 ± 0.009	1.073 ± 0.009
Ba	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bi	0.087 ± 0.004	0.082 ± 0.004	0.078 ± 0.002	0.117 ± 0.006	0.110 ± 0.006	0.109 ± 0.003	0.104 ± 0.006	0.121 ± 0.006	0.102 ± 0.003

[a] The values are expressed in mg L^{-1}.

nitric acid was added. A final dilution to 10 mL with distilled water was made before sample introduction in the measurement systems.

ICP-OES Determination. The operating conditions of the ICP-OES equipment are summarized in **Table 1**. The calibration standards were prepared from a multielemental standard solution and a lanthanide standard solution in 0.5% nitric acid. Two calibration sets were prepared, one for digested samples and a second one for diluted samples. In the last case, a final concentration of 1.25% (v/v) of ethanol was assured in standard solutions, in order to compensate for signal intensity differences caused by surface tension, density, and viscosity during sample nebulization and also changes in the plasma stability and reflected power due to the presence of dissolved organic compounds in undigested diluted samples.

The calibration range for all 41 elements evaluated at trace level (Sc,Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, As, Ba, Be, Bi, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Na, Sr, Tl, Ti, V, and Zn) was from 0.01 to 0.5 mg L^{-1} and for the highly concentrated elements (Ca, Fe, Mg, Mn, K, and Na) till 25 mg L^{-1}.

ICP-MS Determination. ICP-MS data were obtained by using the Total Quant approach, which offers semiquantitative data that, as has been indicated previously, are in good agreement with quantitative ones obtained by using external calibration (*17*). The Total Quant approach has been successfully applied for the analysis of trace metals in wine samples (*18, 24*), and thus, it could be used to evaluate the accuracy of proposed procedures after different sample pretreatments.

A daily solution containing 10 μg L^{-1} of Ba and 1 μg L^{-1} Mg, Al, Cr, Mn, Cu, Rh, Cd, In, Ce, Pb, and Th was used to optimize the operating conditions (see **Table 1**). The radio frequency (RF) power, plasma gas, auxiliary gas, nebulizer gas flow rates, and lens voltage were automatically selected by the instrument during the optimization step. The rest of the instrumental conditions were fixed in the recommended values. A full mass spectrum (*m/z* = 6−15, 19−39, 42−210, 230−240) was obtained by full mass range scanning. A reference response table (Perkin-Elmer Total Quant III) was updated with the multielement (As, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Be, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, Tl, V, and Zn) standard solution at the 10 μg L$^-$ concentration level. This solution was employed for the analysis of previously digested samples. In the case of diluted sample analysis, the aforementioned multielemental standard solution was prepared with a final concentration of 1.25% v/v ethanol.

RESULTS AND DISCUSSION

Optimization of Experimental Parameters for ICP-OES Determination of Diluted Wine Samples. The effect of experimental conditions, such as RF power, sample aspiration flow rate, and sample dilution factor, was evaluated in order to improve the sensitivity of ICP-OES measurements.

The sensitivity of some representative elements (La, Al, Fe, and Zn) was used as response function, evaluating the effect of the aforementioned experimental conditions in a multiparametric way through a central composite design of three factors consisting of 20 combinations in a single block (8 cubic points with 6 center points in cube and 6 axial points with 0 axial center points).

All of the experiments were performed in a random order to avoid trends in data. Analytical sensitivity is mostly affected by the selected parameters and because of that, other parameters, such as auxiliary gas flow rate, sample uptake, and rinse time (with relatively small effects), were adjusted to the fixed values selected to avoid memory effects.

The graphical inspection of the surfaces generated in contour plots, which represent analyte sensitivity to RF, percentage of ethanol, and aspiration flow rate, is the most immediate way of concluding the optimum conditions.

It should be highlighted that plasma shut down when using small dilution factors combined with high values of sample aspiration flow rate and low values of RF power because of the presence of a high concentration of ethanol in the system.

As can be seen in **Figure 1**, the analytical sensitivity increases on increasing RF power. It means that excitation and ionization processes are favored by increasing power. However, if excitation power is set at the limit of the equipment (1500 W), the repeatability of the measurements may be altered because of an increase in the noise level and the background signal.

Taking into consideration that by applying a fixed dilution factor to all wine samples different ethanol contents in the final solution can be obtained, it is necessary to select the experimental conditions to obtain the same response for a relatively wide range of ethanol, to guarantee the robustness of the recommended procedure.

The use of a dilution factor of 1:10 of wine samples provides ethanol contents that vary from 1.2 to 1.42% v/v, and the sensitivity of target elements remains constant in the aforementioned range, as can be seen in **Figure 1**. Therefore, a dilution factor of 1:10, a RF power of 1400 W, and a sample aspiration flow rate of 1.1 mL min^{-1} were selected for further experiments

4948   *J. Agric. Food Chem.,* Vol. 56, No. 13, 2008

Gonzálvez et al.
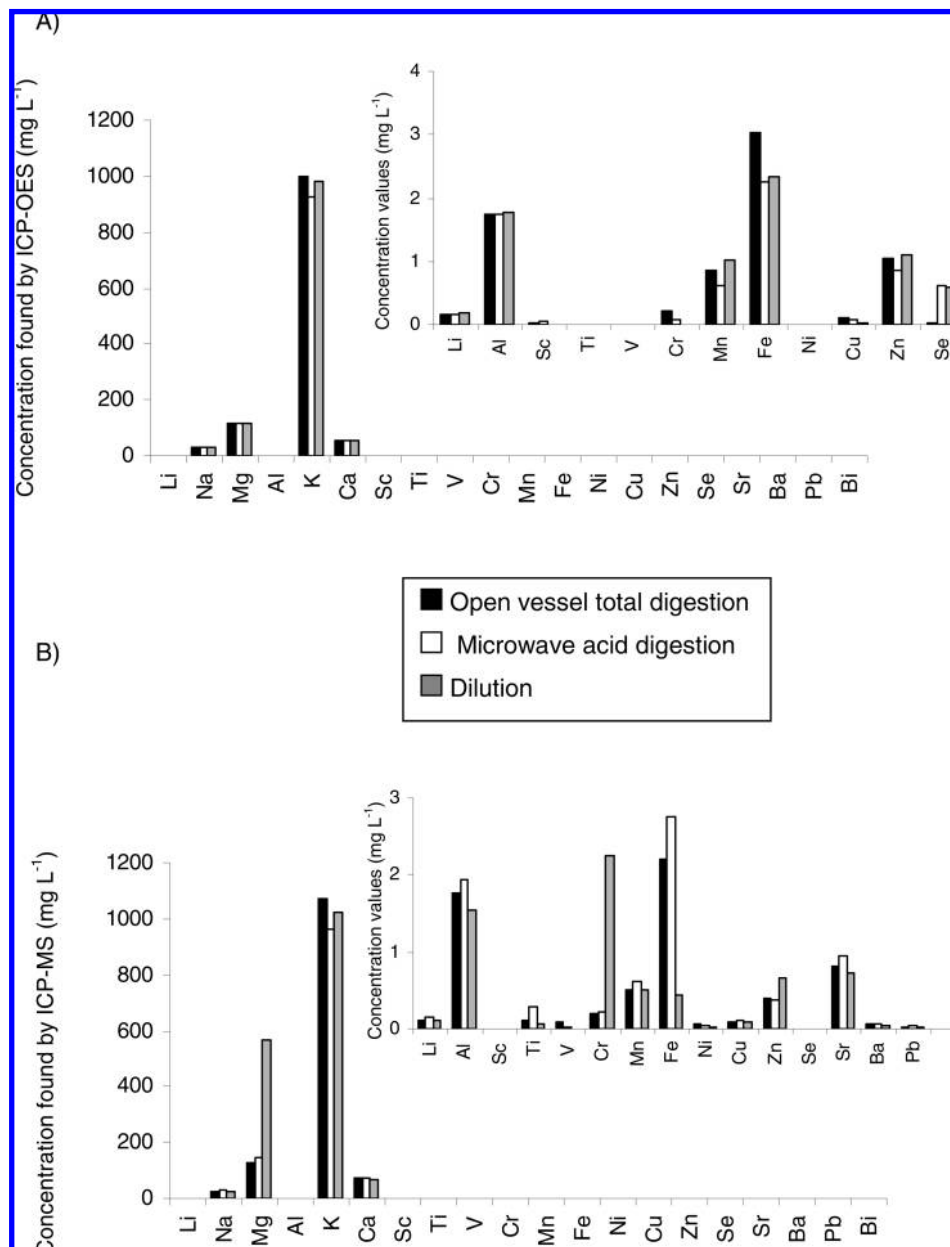
Figure 2. Mean elemental composition of wine samples analysed by (**A**) ICP-OES and (**B**) ICP-MS after different sample pretreatments.

as a compromise between the sensitivity achieved and the sample dilution factor necessary to carry out the measurements using a common external calibration line for all samples analyzed.

In the case of the analysis of previously digested samples, experimental conditions available for aqueous solutions are enough to obtain sensitive and precise data.

Analytical Features of ICP-OES and ICP-MS Procedures.
The analytical characteristics of ICP-OES and ICP-MS measurements made after both, sample digestion and sample dilution are shown in **Table 2**. The limit of detection in ICP-MS was calculated as the concentrations corresponding to signals equal to three-times the standard deviation of a 0.5 μg L^{-1} solution signal in the case of aqueous ethanolic solutions and from the dilution of this standard till a number of counts compatible with the blank ones for acid solutions was reached. For ICP-OES measurements, the LOD was calculated as the concentrations corresponding to signals equal to three-times the standard deviation of a blank solution signal (10 replicates). The

repeatability was calculated as the relative standard deviation (%RSD), for a multielemental standard solution of 0.5 and 10 μg L^{-1} ($n = 10$), for ICP-MS and ICP-OES, respectively.

Effect of the Sample Treatment in ICP-OES Determination. The elemental composition of 12 different wine samples was determined by ICP-OES using the following emission lines indicated in parentheses: Li (670.784 nm), Be (313.107 nm), Na (589.592 nm), Mg (285.213 nm), Al (396.153 nm), K (766.490 nm), Ca (317.933 nm), Sc (361.383 nm), Ti (334.940nm), V (290.880 nm), Cr (267.716 nm), Mn (257.610 nm), Fe (238.204 nm), Co (228.616 nm), Ni (231.604 nm), Cu (327.393 nm), Zn (206.200 nm), As (188.979 nm), Se (196.026 nm), Sr (407.771 nm), Y (371.029 nm), Mo (202.031 nm), Cd (228.616 nm), Ba (233.527 nm), La (408.672 nm), Ce (413.764 nm), Pr (390.844 nm), Nd (406.109 nm), Sm (359.260 nm), Eu (381.967 nm), Gd (342.247 nm), Tb (350.917 nm), Dy (353.170 nm), Ho (345.600 nm), Er (337.271 nm), Tm (313.126 nm), Yb (328.937 nm), Lu (261.542 nm), Tl (190.801 nm), Pb (220.353 nm), and Bi (223.061 nm). The elements found and
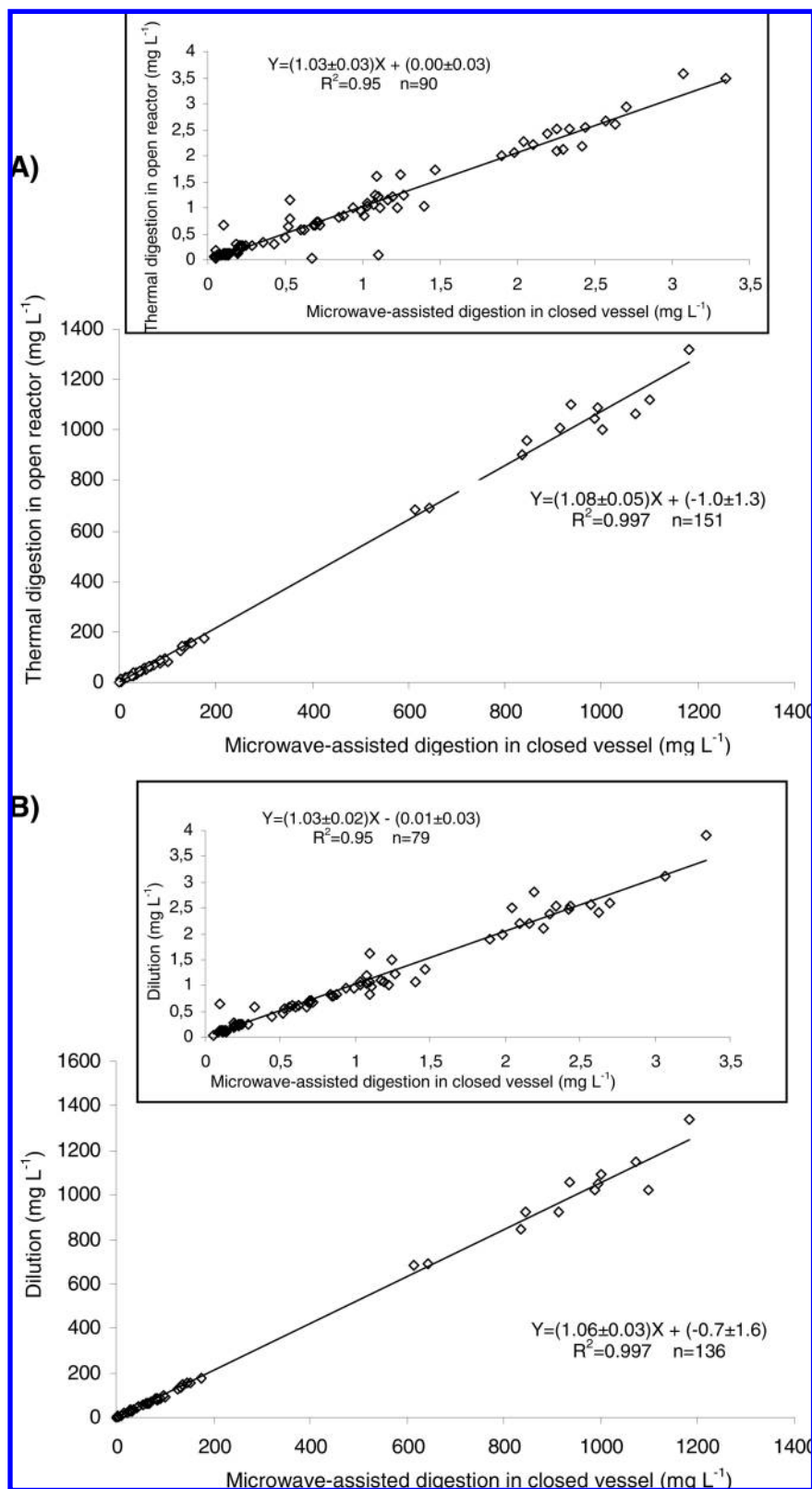
Figure 3. Regression line between results obtained by ICP-OES for the elemental composition of wines after sample treatment by (**A**) acid digestion in open vessel (*y*) plotted against those found by microwave-assisted acid digestion (*x*) and (**B**) sample dilution (*y*) plotted against those found by microwave-assisted acid digestion (*x*).

their concentrations in the different samples considered are summarized in **Table 3**. Samples contain high concentrations of Al, K, Ca, Mg, and Fe combined with the amounts of Ti, which can cause significant background enhancement in many regions of the spectrum and give rise to serious line overlapping interferences in the determination of trace elements as Tl. The

concentration of K in wine samples provides an intensity which saturates the response of the instrument for the three treatments proposed. Thus, it was necessary to dilute the final solutions with an additional factor of 1:10.

Microwave-Assisted Digestion. As can be seen in **Table 3**, ICP-OES provided data on 11 elements, Li, Na, Mg, Al, K,

Table 4. Data of the Elemental Composition of Wines Obtained by ICP-MS after Different Sample Pretreatments[a]

| | D.O. Valencia 1 | | | D.O. Valencia 2 | | | D.O. Valencia 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.131 ± 0.006	0.31 ± 0.01	0.117 ± 0.008	0.137 ± 0.006	0.37 ± 0.01	0.163 ± 0.008	0.112 ± 0.006	0.12 3 ± 0.006	0.117 ± 0.008
Na	27 ± 1	29 ± 1	23 ± 1	30 ± 1	33 ± 1	28 ± 1	12 ± 0.7	17 ± 0.7	12 ± 1
Mg	88 ± 3	94 ± 3	259 ± 7	95 ± 3	100 ± 3	208 ± 7	58 ± 3	88 ± 3	552 ± 7
Al	1.3 ± 0.2	1.6 ± 0.2	0.970 ± 0.09	1.3 ± 0.2	1.7 ± 0.2	1.09 ± 0.1	1.1 ± 0.2	1.7 ± 0.2	0.81 ± 0.08
K	994 ± 30	940 ± 30	967 ± 20	922 ± 30	993 ± 30	987 ± 20	710 ± 21	653 ± 21	698 ± 10
Ca	50 ± 1	51 ± 1	37 ± 1	54 ± 1	55 ± 1	30 ± 1	58 ± 1	61 ± 1	60 ± 1
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	0.044 ± 0.001	0.338 ± 0.001	0.051 ± 0.005	0.072 ± 0.001	0.301 ± 0.001	0.052 ± 0.005	0.04 ± 0.001	0.345 ± 0.001	0.073 ± 0.007
V	0.04 ± 0.02	0.012 ± 0.006	<LOD	0.19 ± 0.009	0.012 ± 0.006	<LOD	0.13 ± 0.009	<LOD	<LOD
Cr	0.18 ± 0.01	0.17 ± 0.01	14 ± 1	0.12 ± 0.01	0.16 ± 0.01	1.02 ± 0.08	0.14 ± 0.01	0.11 ± 0.01	1.47 ± 0.08
Mn	0.52 ± 0.03	0.51 ± 0.03	0.45 ± 0.02	0.48 ± 0.03	0.50 ± 0.03	0.35 ± 0.02	0.29 ± 0.01	0.36 ± 0.02	0.29 ± 0.02
Fe	2.2 ± 0.1	2.0 ± 0.1	0.59 ± 0.05	2.1 ± 0.1	2.4 ± 0.1	0.80 ± 0.07	1.9 ± 0.1	2.4 ± 0.1	0.39 ± 0.03
Ni	0.022 ± 0.001	0.062 ± 0.001	<LOD	0.013 ± 0.001	0.022 ± 0.001	<LOD	<LOD	<LOD	<LOD
Cu	0.37 ± 0.01	0.38 ± 0.01	0.38 ± 0.04	0.29 ± 0.01	0.30 ± 0.01	0.29 ± 0.04	0.04 ± 0.01	0.04 ± 0.01	0.02 ± 0.04
Zn	0.21 ± 0.01	0.21 ± 0.01	0.19 ± 0.01	0.25 ± 0.01	0.23 ± 0.01	0.26 ± 0.02	0.10 ± 0.005	0.07 ± 0.003	0.18 ± 0.01
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	0.83 ± 0.01	0.92 ± 0.01	0.63 ± 0.01	0.92 ± 0.01	1.06 ± 0.02	0.94 ± 0.01	0.67 ± 0.01	0.77 ± 0.01	0.44 ± 0.01
Ba	0.109 ± 0.003	0.098 ± 0.003	0.042 ± 0.003	0.118 ± 0.003	0.114 ± 0.003	0.072 ± 0.005	0.064 ± 0.001	0.071 ± 0.001	0.034 ± 0.002
Pb	0.064 ± 0.002	0.087 ± 0.002	0.065 ± 0.003	0.041 ± 0.001	0.057 ± 0.001	0.042 ± 0.002	0.043 ± 0.001	0.034 ± 0.001	0.029 ± 0.001
Bi	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

| | D.O. Utiel Requena 1 | | | D.O. Utiel Requena 2 | | | D.O. Utiel Requena 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.0070 ± 0.0003	0.0165 ± 0.0008	0.0051 ± 0.0003	0.0093 ± 0.0004	0.0256 ± 0.0001	0.0105 ± 0.0005	0.0090 ± 0.0004	0.0258 ± 0.0001	0.0100 ± 0.0005
Na	23 ± 1	56 ± 3	24 ± 1	17 ± 1	37 ± 2	23 ± 1	29 ± 1	30 ± 1	28 ± 1
Mg	57 ± 2	139 ± 5	500 ± 7	59 ± 2	130 ± 5	643 ± 8	95 ± 5	104 ± 5	643 ± 8
Al	1.0 ± 0.1	2.3 ± 0.3	0.81 ± 0.08	1.0 ± 0.1	2.0 ± 0.3	1.0 ± 0.1	1.6 ± 0.3	1.6 ± 0.3	1.3 ± 0.1
K	1016 ± 30	994 ± 30	1007 ± 20	968 ± 30	864 ± 25	976 ± 20	928 ± 30	1042 ± 30	1035 ± 20
Ca	35 ± 1	35 ± 1	32 ± 1	22 ± 1	37 ± 1	43 ± 1	36 ± 1	39 ± 1	43 ± 1
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	0.056 ± 0.001	0.284 ± 0.001	0.078 ± 0.007	0.049 ± 0.001	0.247 ± 0.001	0.048 ± 0.004	0.049 ± 0.001	0.247 ± 0.001	0.048 ± 0.004
V	0.138 ± 0.006	0.088 ± 0.004	0.056 ± 0.002	0.120 ± 0.006	0.025 ± 0.001	0.0177 ± 0.0008	0.120 ± 0.006	0.025 ± 0.001	0.0173 ± 0.0008
Cr	0.062 ± 0.001	0.126 ± 0.001	1.3 ± 0.1	0.082 ± 0.001	0.123 ± 0.001	0.88 ± 0.07	0.136 ± 0.001	0.122 ± 0.001	0.88 ± 0.07
Mn	0.29 ± 0.01	0.40 ± 0.02	0.31 ± 0.01	0.31 ± 0.02	0.50 ± 0.02	0.40 ± 0.01	0.32 ± 0.02	0.49 ± 0.02	0.41 ± 0.01
Fe	2.3 ± 0.1	3.03 ± 0.1	0.564 ± 0.05	2.4 ± 0.1	2.5 ± 0.1	0.377 ± 0.03	2.4 ± 0.1	2.5 ± 0.1	0.373 ± 0.03
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.014 ± 0.001	0.013 ± 0.001	<LOD
Cu	0.042 ± 0.001	0.051 ± 0.001	0.035 ± 0.003	0.021 ± 0.001	0.034 ± 0.001	<LOD	0.029 ± 0.001	0.033 ± 0.001	<LOD
Zn	0.098 ± 0.005	0.081 ± 0.004	0.20 ± 0.01	0.078 ± 0.004	0.077 ± 0.004	0.21 ± 0.01	0.078 ± 0.004	0.077 ± 0.004	0.21 ± 0.01
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	0.256 ± 0.005	0.321 ± 0.006	0.186 ± 0.003	0.334 ± 0.006	0.389 ± 0.007	0.266 ± 0.005	0.334 ± 0.006	0.389 ± 0.007	0.276 ± 0.005
Ba	0.057 ± 0.001	0.068 ± 0.002	0.034 ± 0.001	0.058 ± 0.001	0.075 ± 0.002	0.044 ± 0.003	0.058 ± 0.001	0.050 ± 0.001	0.044 ± 0.003
Pb	0.029 ± 0.001	0.045 ± 0.002	0.027 ± 0.001	0.0182 ± 0.0007	0.031 ± 0.001	0.0182 ± 0.0009	0.0186 ± 0.0007	0.0212 ± 0.0008	0.0183 ± 0.0009
Bi	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

| | Fontanars Dels Alforins 1 | | | Fontanars Dels Alforins 2 | | | Fontanars Dels Alforins 3 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.113 ± 0.005	0.134 ± 0.006	0.11 ± 0.01	0.122 ± 0.006	0.150 ± 0.007	0.12 ± 0.01	0.129 ± 0.006	0.164 ± 0.008	0.12 ± 0.01
Na	21 ± 1	28 ± 1	21 ± 1	35 ± 2	34 ± 2	38 ± 1	30 ± 1	30 ± 1	30 ± 1
Mg	186 ± 7	133 ± 5	899 ± 26	194 ± 7	145 ± 5	1106 ± 33	108 ± 4	190 ± 7	1037 ± 31
Al	2.0 ± 0.3	2.1 ± 0.3	2.5 ± 0.2	2.8 ± 0.4	2.0 ± 0.3	2.5 ± 0.2	2.9 ± 0.4	2.4 ± 0.3	2.6 ± 0.2
K	1046 ± 31	991 ± 30	1058 ± 20	1189 ± 31	1048 ± 31	1083 ± 20	1091 ± 31	921 ± 30	854 ± 10
Ca	48 ± 1	53 ± 1	40 ± 1	52 ± 1	55 ± 1	46 ± 1	77 ± 1	77 ± 1	78 ± 1
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	0.052 ± 0.001	0.252 ± 0.001	0.059 ± 0.005	0.055 ± 0.001	0.295 ± 0.001	0.060 ± 0.006	0.046 ± 0.001	0.365 ± 0.001	0.045 ± 0.004
V	0.078 ± 0.003	<LOD	<LOD	0.066 ± 0.003	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	0.109 ± 0.001	0.184 ± 0.001	1.02 ± 0.08	0.323 ± 0.001	0.371 ± 0.001	1.16 ± 0.09	0.992 ± 0.001	0.906 ± 0.001	1.97 ± 0.09
Mn	1.30 ± 0.07	0.57 ± 0.03	1.36 ± 0.05	0.62 ± 0.04	0.69 ± 0.04	0.46 ± 0.01	0.52 ± 0.03	0.87 ± 0.05	0.49 ± 0.01
Fe	2.9 ± 0.01	2.6 ± 0.01	0.36 ± 0.03	2.7 ± 0.01	2.7 ± 0.01	0.45 ± 0.04	2.3 ± 0.01	2.5 ± 0.01	0.27 ± 0.02
Ni	0.046 ± 0.001	0.043 ± 0.001	0.025 ± 0.001	0.079 ± 0.001	0.074 ± 0.001	<LOD	0.479 ± 0.001	0.404 ± 0.001	0.116 ± 0.008
Cu	0.169 ± 0.001	0.179 ± 0.001	0.18 ± 0.02	0.030 ± 0.001	0.035 ± 0.001	<LOD	0.098 ± 0.001	0.080 ± 0.001	0.061 ± 0.006
Zn	0.79 ± 0.03	0.74 ± 0.03	0.36 ± 0.02	<LOD	<LOD	<LOD	0.67 ± 0.03	0.63 ± 0.03	0.41 ± 0.03
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	0.87 ± 0.01	0.82 ± 0.01	0.89 ± 0.01	1.54 ± 0.03	1.86 ± 0.03	1.42 ± 0.03	2.79 ± 0.05	2.71 ± 0.05	2.72 ± 0.05
Ba	0.044 ± 0.001	0.061 ± 0.001	0.033 ± 0.002	0.057 ± 0.001	0.075 ± 0.001	0.042 ± 0.002	0.040 ± 0.001	0.060 ± 0.001	0.024 ± 0.001
Pb	0.058 ± 0.002	0.058 ± 0.002	0.050 ± 0.002	0.0175 ± 0.0007	0.0222 ± 0.0008	0.0103 ± 0.0005	0.033 ± 0.001	0.035 ± 0.001	0.0193 ± 0.0009
Bi	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Elemental Analysis of Wines

J. Agric. Food Chem., Vol. 56, No. 13, 2008 **4951**

Table 4. Continued

| | Fontanars Dels Alforins 4 | | | Fontanars Dels Alforins 5 | | | Fontanars Dels Alforins 6 | | |
| | acid digestion | | | acid digestion | | | acid digestion | | |
	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution	open vessel	closed vessel	dilution
Li	0.21 ± 0.01	0.23 ± 0.01	0.21 ± 0.01	0.115 ± 0.005	0.139 ± 0.005	0.115 ± 0.008	0.118 ± 0.005	0.142 ± 0.005	0.121 ± 0.008
Na	28 ± 1	28 ± 1	27 ± 1	17 ± 1	18 ± 1	16 ± 1	46 ± 2	46 ± 2	45 ± 1
Mg	151 ± 6	153 ± 1	350 ± 10	210 ± 8	216 ± 8	175 ± 5	226 ± 8	228 ± 8	423 ± 12
Al	2.9 ± 0.4	2.9 ± 0.4	2.010 ± 0.2	1.65 ± 0.2	1.79 ± 0.2	1.5 ± 0.1	1.3 ± 0.1	1.0 ± 0.1	1.2 ± 0.1
K	1530 ± 40	1325 ± 40	1390 ± 20	1142 ± 40	702 ± 20	742 ± 10	1310 ± 40	1042 ± 30	1130 ± 20
Ca	134 ± 1	135 ± 1	130 ± 1	143 ± 1	148 ± 1	146 ± 1	133 ± 1	133 ± 1	130
Sc	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ti	0.271 ± 0.001	0.303 ± 0.001	0.042 ± 0.004	0.273 ± 0.001	0.256 ± 0.001	0.052 ± 0.005	0.267 ± 0.001	0.274 ± 0.001	0.17 ± 0.01
V	0.090 ± 0.004	<LOD	<LOD	<LOD	<LOD	<LOD	0.086 ± 0.004	<LOD	<LOD
Cr	0.060 ± 0.001	0.143 ± 0.001	1.2 ± 0.1	0.073 ± 0.001	0.175 ± 0.001	0.70 ± 0.05	0.185 ± 0.001	0.153 ± 0.001	1.1 ± 0.1
Mn	0.35 ± 0.02	0.74 ± 0.04	0.47 ± 0.01	0.77 ± 0.04	1.29 ± 0.07	0.71 ± 0.04	0.35 ± 0.02	0.58 ± 0.03	0.42 ± 0.01
Fe	0.928 ± 0.001	3.0 ± 0.1	0.18 ± 0.01	1.4 ± 0.1	3.2 ± 0.1	0.35 ± 0.03	2.5 ± 0.1	4.0 ± 0.1	0.57 ± 0.05
Ni	0.014 ± 0.001	0.027 ± 0.001	0.014 ± 0.001	0.017 ± 0.001	0.020 ± 0.001	<LOD	0.035 ± 0.001	0.018 ± 0.001	<LOD
Cu	0.021 ± 0.001	0.040 ± 0.001	<LOD	0.011 ± 0.001	0.018 ± 0.001	<LOD	0.030 ± 0.001	0.041 ± 0.001	0.020 ± 0.002
Zn	0.051 ± 0.002	0.110 ± 0.006	0.113 ± 0.009	2.3 ± 0.1	2.0 ± 0.1	5.6 ± 0.4	0.096 ± 0.004	0.128 ± 0.006	0.209 ± 0.009
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	0.320 ± 0.006	0.53 ± 0.01	0.263 ± 0.005	0.57 ± 0.01	0.91 ± 0.01	0.389 ± 0.002	0.43 ± 0.01	0.64 ± 0.01	0.334 ± 0.002
Ba	0.0302 ± 0.0009	0.044 ± 0.001	0.023 ± 0.001	0.064 ± 0.002	0.086 ± 0.002	0.046 ± 0.003	0.049 ± 0.001	0.063 ± 0.002	0.035 ± 0.002
Pb	0.0167 ± 0.0006	0.025 ± 0.001	<LOD	0.0196 ± 0.0006	0.027 ± 0.001	0.0163 ± 0.0008	0.0173 ± 0.0006	0.039 ± 0.001	0.024 ± 0.001
Bi	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

[a] The values are expressed as mg L^{-1}.

Ca, Mn, Fe, Zn, Se, and Sr, in all wine samples analyzed. Moreover Ba, Sc, Cr, Cu, and Bi were also detected in the main part of Utiel-Requena P.D.O. and those from Fontanars dels Alforins wine samples. Elements such as Ti, V, Ni, Cd, and Pb were not detected in the samples considered.

Open Vessel Total Digestion. By using open vessel sample digestion treatment, data was obtained on 10 elements, Li, Na, Mg, Al, K, Ca, Mn, Fe, Zn, and Sr, in all samples analyzed and additional data on Ba, Se, Cr, and Cu in some samples. Bi was only quantified in Fontanars dels Alforins wines. In order to have a general point of view, the average of results obtained for the 12 different wine samples obtained after a given sample pretreatment was used (see **Figure 2**); however, the data of individual analysis of each element in each sample were collected for the comparison of the different sample pretreatments. On comparing those data with those found after microwave-assisted digestion, it can be seen that comparable results were found for Li, Na, Mg, Al, K, Ca, Mn, Fe, and Sr. However, Se concentration values in all the samples analyzed were lower than those obtained by the other pretreatments and in some cases lower than the LOD of the technique, probably due to analyte losses during the digestion process in the open system. Therefore, it can be concluded that microwave-assisted digestion of wine permits the accurate determination of more elements than the use of a complete digestion using convective heating in an open vessel in spite of the fact that the later treatment provides a low sample dilution (1:5).

Dilution. An average number of 12 elements were quantified in the considered samples after dilution (see **Figure 2**). However, it must be taken into consideration that the direct measurement of 1:10 wine diluted samples involves the presence of the whole sample matrix during the measurement step. It could be the reason for finding Pb, at 100 ppb levels, in 5 samples for which sample digestion procedures provided undetectable data; thus, the Pb values could be due to background or matrix artifacts.

However, data found for Bi and Se are in good agreement with those obtained after microwave-assisted digestion.

Comparison of Sample Treatment Procedures in Order to Analyze Wines by ICP-OES. Results obtained for the analysis of all quantified elements in 12 different wine samples after complete acid digestion in an open vessel (y) were plotted against those found after microwave-assisted acid digestion (x) (see **Figure 3A**), providing the following equation: $y = (1.08 \pm 0.05)x - (1.0 \pm 1.3)$ with $R^2 = 0.997$ ($n = 151$), which has intercept and slope values comparables to 0 and 1, respectively. The inset of the figure shows the aforementioned regression established for elements with concentration values lower than 4 mg L^{-1}, providing an equation of $y = (1.03 \pm 0.03)x + (0.00 \pm 0.03)$ with $R^2 = 0.95$ ($n = 90$).

The regression between the values obtained for all quantified elements in the 12 samples considered by dilution (y) and those obtained by microwave-assisted acid digestion (x) provided a regression line $y = (1.06 \pm 0.03)x - (0.7 \pm 1.6)$, with $R^2 = 0.997$ ($n = 136$) (see **Figure 3B**), which also has intercept and slope values comparable to 0 and 1, respectively. The regression of the concentration values found for elements with concentrations lower than 4 mg L^{-1} can bee seen in the inset of **Figure 3B** and provided a regression line of $y = (1.03 \pm 0.02)x - (0.01 \pm 0.03)$ with $R^2 = 0.95$ ($n = 79$).

In short, it can be concluded that for the main part of elements and samples analyzed the three sample preparation methods provided comparable results. However, it is clear that total digestion in an open vessel does not allow Se determination and that direct measurement of diluted wines can provide excess errors in the estimation of Pb by ICP-OES and because of that microwave-assisted digestion could be (from the accuracy point of view) the method of choice.

Effect of the Wine Sample Pretreatments on ICP-MS Determination. The elemental composition of the 12 wine samples considered was established by ICP-MS. The elements found and their concentrations in the samples are summarized in **Table 4**.

Se presents spectral interferences, and the determination of this element by conventional ICP-MS is not allowed. The formation of polyatomic ions in the argon plasma causes some interference with some selenium isotopes. A major interference is the formation of the dimer $^{40}Ar_2^+$, which overlaps the mass signal with the most abundant selenium isotope, ^{80}Se. Furthermore, it must be noticed that we did not find Sc nor Bi in any of samples analyzed and that it disagrees with data obtained by ICP-OES.
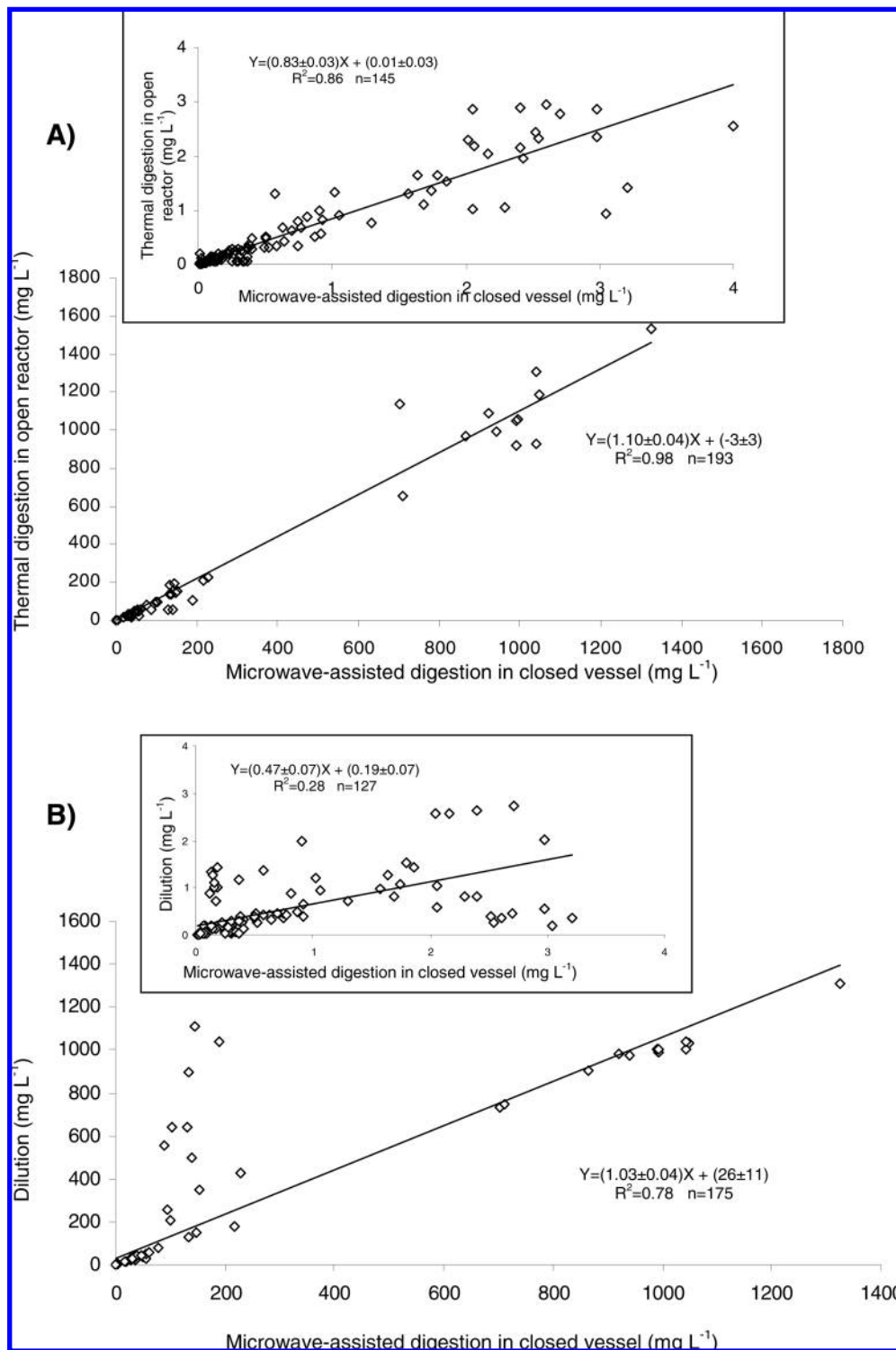
Figure 4. Regression line between results obtained by ICP-MS for the elemental composition of wines after sample treatment by (**A**) acid digestion in an open vessel (*y*) plotted against those found by microwave-assisted acid digestion (*x*) and (**B**) sample dilution (*y*) plotted againt those found by microwave-assisted acid digestion (*x*).

Microwave-Assisted Digestion. Fifteen elements, Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Sr, Ba, and Pb, were quantified in all of the samples assayed by ICP-MS. Additionally, Zn and V were determined in the main part of samples, thus offering additional information to that found by ICP-OES.

Open Vessel Digestion. An average number of 16 elements were quantified on ICP-MS after complete digestion of samples in an open vessel. It includes V in all of the samples, compared with data found after microwave-assisted digestion. However,

as can be seen in **Figure 2**, V data found by open vessel digestion are overestimated compared to data obtained from the other sample preparation methods assayed.

Dilution. Direct ICP-MS analysis of diluted wine samples offer quantitative data of 13 to 16 elements, probably due to matrix interferences during the measurement step. For Ti, Fe, and Ni, direct measurement of diluted samples provided defect errors as compared with data found after digestion. Otherwise, for Mg and Cr, excess errors were found.

Elemental Analysis of Wines

J. Agric. Food Chem., Vol. 56, No. 13, 2008 **4953**
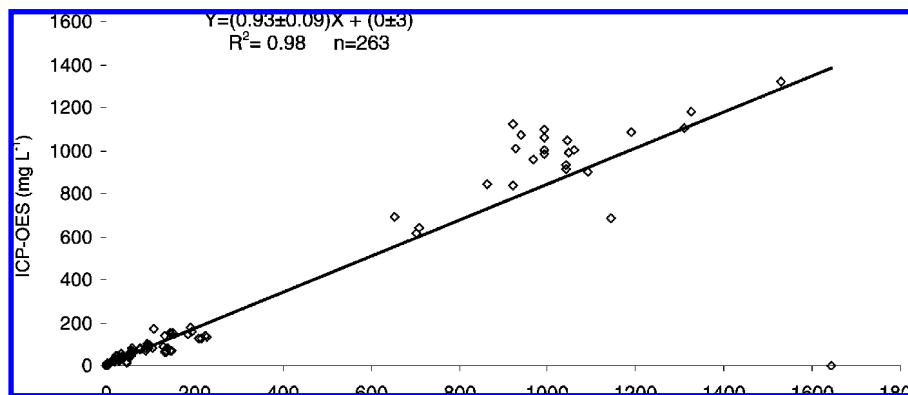
Figure 5. Regression line between results obtained by ICP-OES (*y*) plotted against those found by ICP-MS (*x*) for the elemental analysis of wines.

All of the aforementioned problems can be explained by the presence of alcohol and organic compounds, particularly sugars, which could interfere with ICP-MS measurements by suppressing some signals or creating isobaric interferences (*14*).

Comparison of All Data Reported for ICP-MS Analysis of Wines. Comparable results were obtained between acid digestions in both open and closed vessels for all of the elements with the exception of Ti and Li in several samples, for which microwave-assisted digestion provided higher values than the other two alternative procedures. However, when comparing dilution values with those obtained by digestion, it can be observed that for Mg, Cr, Fe, and Ba the results found were statistically different.

As can be seen in **Figure 4A**, when results obtained for the analysis of wine samples after total acid digestion in and open vessel (*y*) were plotted against those found after microwave-assisted acid digestion (*x*), the following equation $y = (1.10 \pm 0.04)x - (3 \pm 3)$ with $R^2 = 0.98$ (*n* = 193) was found. This line has an intercept and slope values comparable to 0 and 1, respectively. However, the regression between values obtained directly in diluted samples (*y*) and those obtained by microwave-assisted acid digestion (*x*) provided a regression line $y = (1.03 \pm 0.04)x + (26 \pm 11)$, with $R^2 = 0.78$ (*n* = 175), which has an intercept value statistically different from 0, thus indicating the problems arising from matrix effects in direct elemental analysis by ICP-MS of just diluted wine samples (see **Figure 4B**).

Comparison of ICP-OES and ICP-MS Results. A linear least-squares adjustment was applied to results obtained by both assayed techniques, ICP-MS (*x*-axis) and ICP-OES (*y*-axis), after acid digestion treatments. An equation $y = (0.93 \pm 0.09)x + (0 \pm 3)$ (95% confidence level), with a correlation coefficient of $R^2 = 0.98$ (*n* = 263), was obtained (see **Figure 5**). The intercept and slope values were comparable to 0 and 1, respectively, and it demonstrates that, in general, the accuracy of both methodologies is comparable. It is important to highlight that in the wine samples analyzed the number of elements determined by ICP-MS (*15–17*) is higher than those analyzed by ICP-OES (*10–15*) because of the high sensitivity and low detection limits of ICP-MS and that only elements quantified by both techniques were compared in the aforementioned regression.

On comparing the sample pretreatment methodology, the three assayed procedures provide comparable results for the concentration of Li, Na, Mg, Al, K, Ca, Mn, Fe, Zn, and Sr by ICP-OES. Additionally, ICP-MS data found for Cu, Pb, and Ba were comparable. Digestion treatment provided comparable values using both total decomposition in an open system and microwave-assisted treatment for Cu by ICP-OES and for Cr, Ni, and Zn by ICP-MS. Open vessel total digestion provides excess values

for Cr, Mn, Fe, and Zn by ICP-OES and defect values for Se. However, direct measurement of diluted wine samples provided uncomparable results with the digestion treatment for Mn, Cu, Pb, Zn, Ba, and Bi in ICP-OES and for Mg, Cr, Fe, Ni, and Zn by ICP-MS.

In short, it must be concluded that both assayed techniques are complementary for determining the elemental composition of wines.

From data obtained through this study, it can be evidenced that direct dilution of samples creates problems for matrix-sensitive elements; thus, a previous digestion of samples is recommended.

Total sample digestion can provide analyte losses and complicates ICP-MS analysis by the introduction of perchloric acid. Therefore, microwave-assisted digestion is the method of choice to be used in elemental analysis of wines by ICP-based techniques.

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4954 *J. Agric. Food Chem.,* Vol. 56, No. 13, 2008

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