Available online at www.sciencedirect.com
SCIENCE DIRECT
Talanta 68 (2006) 1640–1647
Talanta
www.elsevier.com/locate/talanta

Detection of bias errors in ETAAS Determination of copper in beer and wine samples

M. Llobat-Estellés *, A.R. Mauri-Aucejo, R. Marin-Saez

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

Received 19 April 2005; received in revised form 27 July 2005; accepted 9 August 2005
Available online 21 September 2005

Abstract

A method that evidences changes in the shape of the absorbance profiles obtained by graphite furnace atomic absorption spectrometry (ETAAS) is proposed. The method is based upon the apparent content curves model previously described for molecular spectroscopy and it permits the detection of possible sources of bias errors. Moreover, a procedure that allows to detect the existence of constant and/or proportional errors is also described. Both models has been applied to the determination of copper in wine and beer samples with and without pre-treatment of the samples. Results obtained evidence the usefulness of the proposed models.

Keywords: ETAAS; Bias errors; Apparent content curves; Wine; Beer

1. Introduction

Alcoholic beverages can contain several metallic elements that come from raw materials, crop treatment or manufacturing processes. These elements may be harmful and even lethal above certain concentration levels, and moreover, some of them can affects negatively the organoleptic characteristics and the overall quality of a given product [1]. Thus, determination of trace elements over this matrix is of clear interest.

Thereby, for very popular alcoholic beverages as wine or beer, a great number of methods of determination of minor and major elements has been developed. Described procedures involve determination of toxic elements (Cd, Hg, Pb) or essential elements (Cu, Fe) that are prejudicial at high concentrations.

Particularly, wines contain different amounts of copper as a consequence of its addition for removing sulfidic off-odours. However, high concentration can cause oxidative spoilage of the wine leading to pinking of red wine and browning of white wine as well as haze formation [2]. It is therefore recommended that the total copper be below 0.3–0.5 μg/ml.

To determine copper in wines a lot of procedures based on different analytical techniques have been described being atomic spectroscopy (FAAS, ETAAS, ICP) [3] and electroanalytical techniques [2,4–6] the most widely proposed.

ICP–MS is a multielemental technique widely proposed for a detailed characterization of the elemental composition of wines [7–9]. However, to determine a single element, ETAAS constitutes an excellent tool, which provides high selectivity, high sensitivity and low detection limits [10–12].

Proposed procedures do not imply the previous mineralization of samples and so, digestion procedures are generally obviated. Samples are directly injected after the addition of dilute HNO_3 and the use of matrix modifier is not recommended. Moreover, determination is carried out by the standard addition method [11].

On the other hand, beer is manufactured from natural materials including water, barley and yeast, all of which are potential sources of copper. As the content of copper in beer can contribute to the foaming quality and the flavour enhancement [13], the study of analytical procedures for determination of copper in beer results of particular interest. In this case, similarly to wine samples, the use of atomic spectroscopy [13–18] and electroanalytical techniques [19] have been generally proposed.

Using atomic spectroscopic techniques, most of described procedures include degasification and a previous digestion of

* Corresponding author. Tel.: +34 963544497; fax: +34 963544436.
E-mail address: maria.j.llobat@uv.es (M. Llobat-Estellés).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.08.047

samples by dry ashing or acid treatment with HNO_3 and H_2O_2 often in a microwave oven [14,16,17].

However, several studies indicate that determination of copper by ETAAS can be carried out without a previous digestion of samples. In this way, Svendsen and Lund [13] propose the previous dilution of samples with the aim to avoid the poor reproducibility obtained as a consequence of the remaining ash layer formed in the graphite tube when undiluted beer are injected. The results obtained are in agreement with those obtained after acid mineralization of samples.

Moreover, Viñas et al. [18] describe a procedure, which avoids the previous digestion of samples for the determination of cadmium, aluminium and copper in beer by ETAAS. Samples were prepared by adding nitric acid and hydrogen peroxide that provide an oxidizing environment during atomisation avoiding accumulation of carbonaceous residues and then, the obtaining of high background values. Moreover, for determination of copper the use of ammonium nitrate as matrix modifier is not necessary. Samples are also analysed by a procedure which includes an acid digestion in a microwave oven and the authors conclude that no significant difference between results obtained by using the two sample treatment.

In this work, determination of copper in wine and beer samples by ETAAS and using both direct injection and acid treatment of samples in a microwave oven is carried out. In all cases the atomisation profiles are studied and the characterization curves based into the apparent content curves model (ACCs) obtained.

The apparent content curves were described in 1992 for molecular spectroscopy [20] and they are based on the representation of the parameter F_{λ_i} versus λ_i:

$$F_{\lambda_i} = \frac{(S)_{\lambda_i}}{(\alpha_A)_{\lambda_i}}$$

where $(S)_{\lambda_i}$ and $(\alpha_A)_{\lambda_i}$ are the values of the signal and the coefficient of response (slope of the calibration graph) of the analyte at λ_i, respectively.

These curves allow to ascertain the presence of spectral interferences in a sample since, in the absence of interferences, the ACCs are straight lines with zero slope, being the intercept the concentration of the analyte in the sample. Particularly, these curves indicate if spectra of samples and standards are proportional and so, they show the existence of spectral interferences that modify the shape and/or position of the spectrum of a given analyte.

From this model, several strategies which allow the identification of interferences and the quantification of an analyte in binary [20,21], ternary [22] and multicomponents [23] samples have been developed and applied to different types of samples [24–28].

The adaptation of the model to atomic spectroscopy implies the obtaining of curves similar than ACCs from the atomisation profiles of samples considering, in this case, the time of atomisation as independent variable. These curves are designed as characterization curves.

As it is indicated in the theoretical part, these curves can constitute a good tool for characterizing atomisation profiles. This characterizing is a topic of general interest, as show by the extensive bibliography in the matter [29–34], because the characterization of atomisation profiles can be useful to detect the presence in the sample of substances which modify the shape and position of the atomisation peak.

Moreover, results obtained from characterizing the atomisation profiles by this model can be confirmed applying a new model, which allows for the detection of bias errors in spectroscopic techniques [35]. This model involves signals obtained for different dilutions of the samples and permits to establish the existence of constant or proportional bias errors.

Application of these models to results obtained after the two sample treatments under study (direct injection and acid treatment of the samples in a microwave oven) permit to establish the suitable pre-treatment in each case.

2. Theoretical part

2.1. Characterization of atomising profiles

To obtain the *F*-values corresponding to an atomisation profile, the signals obtained for the sample and a solution of analyte of known concentration at different atomisation times are considered and *F*-values are calculated as:

$$F_{t_i} = \frac{(A^S)_{t_i}}{(A^P)_{t_i}} \quad (1)$$

where $(A^S)_{t_i}$ and $(A^P)_{t_i}$ are the absorbance signals at t_i for the sample and standard, respectively.

Moreover, if the standard addition method is used, the *F*-values can be obtained as follows:

$$F_{t_i} = \frac{(A^S)_{t_i}}{(A^{S+P})_{t_i}} \quad (2)$$

where $(A^{S+P})_{t_i}$ is the absorbance signal provided by a spiked sample (solution of sample with a known amount of analyte added) at t_i.

These signals can be expressed as follows:

$$(A^S)_{t_i} = C_A^S (f_A^S)_{t_i} + \xi_{t_i} \quad (3)$$

$$(A^{S+P})_{t_i} = C_A^S (f_A^S)_{t_i} + C_A^P (f_A^P)_{t_i} + \xi_{t_i} \quad (4)$$

where $(f_A^S)_{t_i}$ and $(f_A^P)_{t_i}$ are the coefficients of response of the analyte, at each time, in the sample and standard, C_A^S and C_A^P their respective concentration and ξ a signal independent of the concentration of the analyte which, moreover, can be dependent or independent of amount of the matrix.

Considering Eqs. (3) and (4), the expression for the *F*-values results:

$$F_{t_i} = \frac{C_A^S (f_A^S)_{t_i} + \xi_{t_i}}{C_A^S (f_A^S)_{t_i} + C_A^P (f_A^P)_{t_i} + \xi_{t_i}} \quad (5)$$

If we consider that signals obtained are only dependent of the presence of the analyte ($\xi = 0$), above expression remains:

$$(F)_{t_i} = \frac{C_A^S (f_A^S)_{t_i}}{C_A^S (f_A^S)_{t_i} + C_A^P (f_A^P)_{t_i}} \quad (6)$$

Moreover, if:

$$(f_A^S)_{t_i} = K (f_A^P)_{t_i} \quad (7)$$

the F_{t_i} acquire a constant value independent of t_i since:

$$(F)_{t_i} = \frac{K C_A^S}{K C_A^S + C_A^P} = \text{constant} \quad (8)$$

In conclusion, $F_{t_i} = f(t_i)$ (characterization curves) will be a straight line with zero slope if signals are only dependent of the amount of the analyte in the samples, and moreover, the coefficient of response for the analyte in samples and standards be identical or proportional.

2.2. Pattern curves

The lack of precision of the experimental points allows to obtain curves which do not fit to the theoretical prediction (straight lines with zero slope). For testing if a experimental curve indicates that both atomisation profiles (sample and spiked sample) can be considered identical, the obtaining of a pattern curve for the analyte is proposed.

This pattern curve is established from the experimental curves obtained from a series ($n + 1$) of different standard solutions of analyte (considering one of them as reference). As it is indicated above, each one of the n curves obtained will be affected by the lack of precision of the experimental conditions, and therefore, it is not possible obtain n identical straight lines. From these curves, a mean curve with their confidence levels is obtained and considered as pattern curve.

In this way, if the $F_{t_i} = f(t_i)$ of the sample under study fits within the confidence bands of the pattern curve, it can be considered that the atomisation profiles of both standard and sample are proportional.

2.3. Obtaining the pattern curve

Firstly, aqueous solutions containing different amounts of analyte are prepared and their atomisation profiles registered.

Next, the time interval of the profiles is worked out calculating the time at which the peak appears (t_{app}) and the time when the transitory signal disappears (t_{end}). For this, t_{app} is considered as the one corresponding to an absorbance signal equal to four times the deviation of blank (S_{blank}) and similarly, the final time (t_{end}) correspond to the same absorbance value after the peak. Moreover, the deviation of the baseline (S_{blank}) is obtained from the background noise bearing the maximum signal variation at times far from the peak and considering that this value corresponds to $5S_{blank}$

Taking one of the profiles as reference, the values of F_{t_i} are calculated as the ratio between the signal of each solution at t_i and the signal at the same time for the solution taken as reference. From these values the curves for each aqueous solution are obtained.

These curves must be straight lines with zero slope and intercept equal to the ratio between the concentration of analyte in each solution and the concentration of analyte in the reference solution. Once obtained, each curve is normalized calculating the $F_{t_i}^n$ values as follows:

$$F_{t_i}^n = \frac{F_{t_i}}{\bar{F}}$$

where F_{t_i} represents each one of the F-values of a curve and $\bar{F} = (1/n) \sum_{t_{app}}^{t_{end}} F_{t_i}$.

Finally, for each time, the standard deviation of the $F_{t_i}^n$ values are obtained and the confidence bands established as $F_{t_i}^{mean} \pm s_{t_i}$, where $F_{t_i}^{mean}$ is the average of $F_{t_i}^n$ and s_{t_i} is their standard deviation.

2.4. Detection of bias errors

As it is indicated above, spectroscopic techniques provide signals which, in presence of different sources of error, can be expressed as follows:

$$A^S = f_A^S C_A^S + \xi \quad (9)$$

where A^S is the absorbance signal of sample, f_A^S the coefficient of response of the analyte in the sample, C_A^S the analyte concentration and ξ a signal independent of the amount of analyte in the sample which constitutes the origin of bias errors. These errors can be of various types: if they vary with the amount of sample, they are called proportional errors, but if they do not change with the amount of sample, they are denominated constant errors.

In this way, previous expression can be written as follows:

$$A^S = f_A^S C_A^S + K + \Psi \quad (10)$$

where K and Ψ are the origin of constant and proportional errors, respectively.

If we prepare different dilutions (i) of the sample, as K is independent of dilution whereas Ψ is dependent of it, to each dilution we will have:

$$(A^S)^i = (f_A^S)^i C_A^S i + K + \Psi^i \quad (11)$$

Therefore, dividing by the slope of the calibration curve obtained for each dilution $(f_A^S)^i$ and by the dilution factor (i), Eq. (11) remains:

$$\frac{(A^S)^i}{(f_A^S)^i i} = C_A^S + (K + \Psi^i) \frac{1}{(f_A^S)^i i} \quad (12)$$

And, for which, if we represent $(A^S)^i/(f_A^S)^i i$ versus $1/(f_A^S)^i i$ we can obtain:

(a) A straight line with zero slope and intercept C_A^S if $K = 0$ and $\Psi = 0$.
(b) A straight line with a slope different to zero and intercept C_A^S if $K \neq 0$ and $\Psi = 0$.
(c) Not straight line if $K = 0$ and $\Psi \neq 0$.
(d) Not straight line if $K \neq 0$ and $\Psi \neq 0$.

In conclusion, only in the absence of bias errors, proportional or constant, a straight line with zero slope is obtained. Moreover, the intercept of this line must coincide with the concentration of analyte in the sample once applied the corresponding factor of dilution.

3. Experimental

3.1. Apparatus and reagents

All data were obtained on a Perkin-Elmer 4100 ZL atomic absorption spectrometer. In all experiments, THGA Perkin-Elmer graphite tubes (BO 504033 (BO 508884)) were used.

Instrumental conditions and the optimised temperature programs of the furnace are summarized in Table 1.

A microwave oven, Samsung M182DN, is also used for the sample treatment.

Stock solution of Cu of 1000 mg/l was prepared by dissolve 1 g of Cu metal in 50 ml of HNO_3 5 M and dilution to 1000 ml with Nanopure water (Barnstead).

Nitric acid utilized was Suprapur (Merck).

3.2. Procedures

For the mineralization of samples, an aliquot of degassed sample (20, 15 or 10 ml) and 3 ml of concentrate nitric acid were placed into a Teflon vessel. The vessels were closed and a three-step programme was set, each step at 40% power for 2 min. The reactors were opened, and in a second stage 2 ml of 30% H_2O_2 was added. The setting was 40% power for 3 min. After cooling at room temperature, the vessels were opened and the solutions filtered if was necessary, finally solutions were transferred to a 25-ml volumetric flask and diluted to volume with Nanopure water.

4. Results and discussion

4.1. Pattern curve of Cu

Different standard solutions with different amounts of Cu up to 200 μg/L are prepared in HNO_3 0.2%. The atomisation profiles under the two instrumental conditions previously indicated are obtained and, considering one of these profiles as reference, the different characterization curves are calculated. From these curves two pattern curves of Cu (corresponding to the two programs of temperature proposed) are obtained following the procedure indicated in Section 2.

Fig. 1 shows the pattern curve of Cu for the two programs of temperature used for the determination of copper in wine and beer samples, respectively.

Table 1
Experimental conditions

Step	Temperature (°C)	Ramp time	Time
Program temperatures for beer samples			
1	110[a]	1	20
2	130[a]	5	30
3	1150[b]	10	5
4	1200[b]	1	5
5	2100[c]	0	5
6	2400[d]	1	5
Background correction	Zeeman effect		
Matrix modifier (only for direct injection)	10 μl of HNO_3 0.2%		
Injection volume of sample	10 μl		
Wavelength	324.8 nm		
Slit	0.7 nm		
Program temperatures for wine samples			
1	110[a]	1	10
2	130[a]	5	15
3	750[b]	10	5
4	800[b]	10	4
5	2100[c]	0	5
6	2450[d]	1	5
Background correction	Zeeman effect		
Matrix modifier (only for direct injection)	10 μl of HNO_3 0.2%		
Injection volume of sample	10 μl		
Wavelength	324.8 nm		
Slit	0.7 nm		

[a] Dry temperature.
[b] Pyrolisis temperature.
[c] Atomization temperature.
[d] Cleaning temperature.

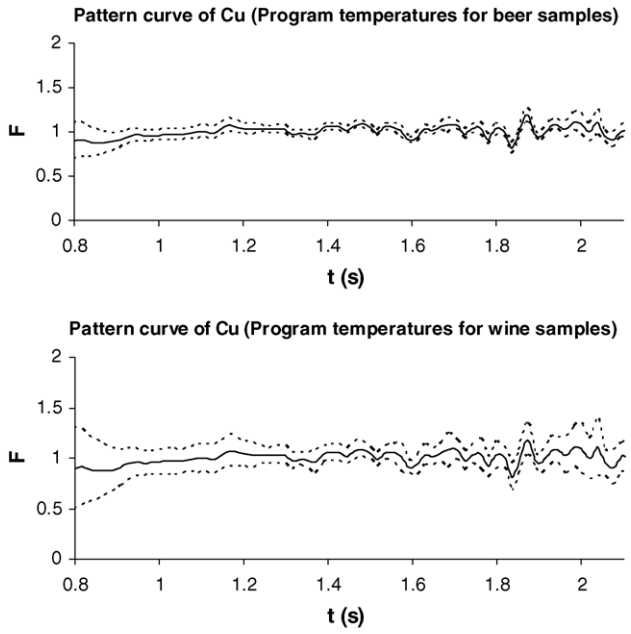

Fig. 1. Apparent content curve pattern obtained from aqueous standard solutions of copper by using both temperature programs. (—) $F_{t_i}{}^{\text{mean}}$; (- - -) $F_{t_i}{}^{\text{mean}} \pm s_{t_i}$.

4.2. Curves for samples of wine and beer

The curves of the samples are obtained from the F-values calculated as follows:

$$F_{t_i} = \frac{(A^{\text{S}})_{t_i}}{(A^{\text{S+P}})_{t_i}}$$

where $(A^{\text{S}})_{t_i}$ is the signal at t_i of a solution of the sample and $(A^{\text{S+P}})_{t_i}$ is the signal of a solution of the sample containing an added amount of copper of 60 μg/L (spiked sample).

Next, the values of F_{t_i} are normalized as it is indicated in Section 2. Finally, considering three replicates of each sample, the curves are obtained from the $F_{t_i}^{\text{mean}} \pm s_{t_i}$ values.

Fig. 2 shows the curves obtained by direct injection for samples of beer, white wine and red wine superimposed with the corresponding pattern curve. As can be seen, the curve corresponding to white wine is into the confidence interval of the pattern curve whereas, for red wine and beer samples the curves are clearly different of the pattern curve.

From these results, it can be deduced that the determination of Cu in wine and beer by ETAAS and direct injection can provide inaccurate results. Then, direct injection for wine and beer samples cannot be advised.

On the other hand, the atomisation profiles and characterization curves obtained after pre-treatment of samples with HNO_3 and H_2O_2 in a microwave oven (Section 3) are also obtained (Fig. 3). In this case, curves obtained overlap with the pattern curve and so, we can be concluded that the profiles of samples and spiked samples for wine and beer samples are not significantly different.

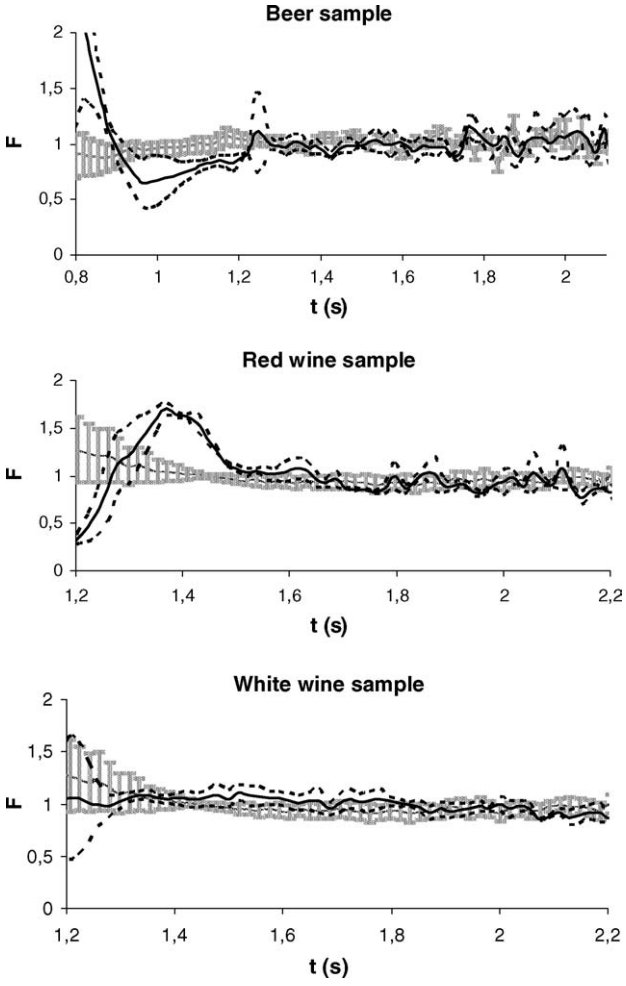

Fig. 2. Apparent content curves obtained by direct injection for different studied matrix: Pattern curve: ( ) $F_{t_i}{}^{\text{mean}} \pm s_{t_i}$; Sample curve: ( ) $F_{t_i}^{\text{mean}} \pm s_{t_i}$.

4.3. Determination of Cu in wines: detection of bias errors

To be able to guarantee the quality of the results, the methodology previously described is applied. In this way, the following experimental procedure is proposed:

(1) Perform different dilutions of the sample.
(2) Obtain for each dilution an addition standard calibration graph using signals of samples and spiked samples for each dilution and calculate the concentration of analyte in each dilution by the standard addition method.
(3) Obtain the graphic corresponding to Eq. (12)
(4) Analyse the representation obtained and, in the case of getting a straight line, compare the value of the intercept with the average concentration obtained from the application of the standard addition method to the different dilutions. If the results coincide, it can be concluded that the determination is free of bias errors.

This procedure was applied to 10 samples of wine as follows:

For each sample, the intercept of the Eq. (12) and the mean concentration provided by the addition standard method are

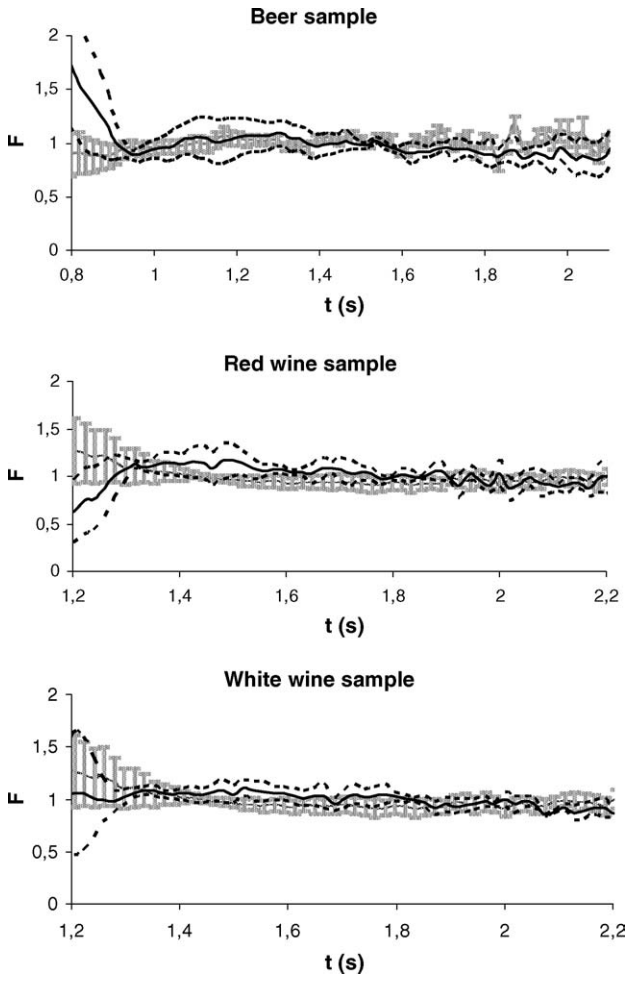

Fig. 3. Apparent content curves obtained after pre-treatment for different studied matrix: Pattern curve: ( ) $F_{t_i}^{\text{mean}} \pm s_{t_i}$; Sample curve: ( ) $F_{t_i}^{\text{mean}} \pm s_{t_i}$.

obtained (Table 2). These values must coincide if the slope of the Eq. (12) is zero and so, for testing statistically the results obtained, the representation of the intercept values versus the mean concentration values is obtained. Then, the joint confidence region for slope and intercept of the straight line is calculated [36] and:

$$F = \frac{(\beta_0 - b_0)^2 + 2\bar{x}(\beta_0 - b_0)(\beta_1 - b_1) + (\sum(x_i^2/n))(\beta_1 - b_1)^2}{2s^2/n}$$

where β_0 and b_0 are the theoretical and experimental values of the intercept, β_1 and b_1 the theoretical and experimental values of the slope, n the number of experimental points y_i versus x_i, $\bar{x}$ the mean value obtained from x_i-values and s^2 the residual variance.

This "F"-value is compared with the F-distribution with 2 and $n-2$ degrees of freedom at the chosen significance level and the results obtained indicate that the intercept and the slope of the straight line are significantly different (Fig. 4). So, the determination of copper in wine samples by ETAAS and direct injection do not provide accurate results. This conclusion is in agreement with the results obtained from the representation of the characterization curves.

This methodology has also applied to results obtained after pre-treatment of samples in a microwave oven. In this case, intercepts and mean values coincide and it can be concluded that results obtained from ETAAS after pre-treatment of samples are accurate.

Moreover, as it was above indicated, if the representation of Eq. (12) is a straight line with a slope different to zero, the intercept coincides with C_A. In this way, the values of intercepts are compared with the mean values obtained after pre-treatment of samples (considered as true values). As it can be seen (Fig. 4), results are not significantly different for all samples.

4.4. Determination of Cu in beer: detection of bias errors

As the atomisation profiles of Cu in beer samples and spiked samples by direct injection do not coincide, we expect that results obtained are inaccurate.

In this way, the same methodology applied to wine samples is developed and the results obtained are shown in Table 3. In all cases, appreciable differences between the mean concentration and the intercept are obtained (Fig. 4). So, determination of Cu in beer by direct injection is not possible.

However, results obtained after the proposed pre-treatment of samples indicate that the slope of the representation of the Eq.

Table 2
Results obtained for Cu in wine samples

Sample	Direct injection		Pretreatment	
	Intercept (μg/l)	Mean concentration (μg/l)[a]	Intercept (μg/l)	Mean concentration (μg/l)[a]
Red wine garnacha Baron de Turis (D.O. València)	84	83 ± 4	92	100 ± 40
Red wine L'Antigon (D.O. València)	159	180 ± 20	153	160 ± 10
Red wine Viña Lucentum (D.O. Alacant)	41	43 ± 9	35	35 ± 5
Red wine Vinyes Roges (D.O. Catalunya)	62	53 ± 8	43	50 ± 10
Red wine Castillo de Liria (D.O. València)	49	51 ± 6	42	42 ± 11
White wine Baron de Turis (D.O. València)	83	95 ± 15	101	90 ± 10
White wine L'Antigon (D.O. València)	293	330 ± 30	346	330 ± 70
White wine Vega Cristina (D.O.La Mancha)	161	150 ± 10	166	150 ± 20
White wine Viña Titon (D.O. Campo de Borja)	70	80 ± 20	86	80 ± 20
White wine Castillo de Liria (D.O. València)	27	32 ± 4	44	39 ± 8

[a] Value obtained as mean of three dilutions of each sample.

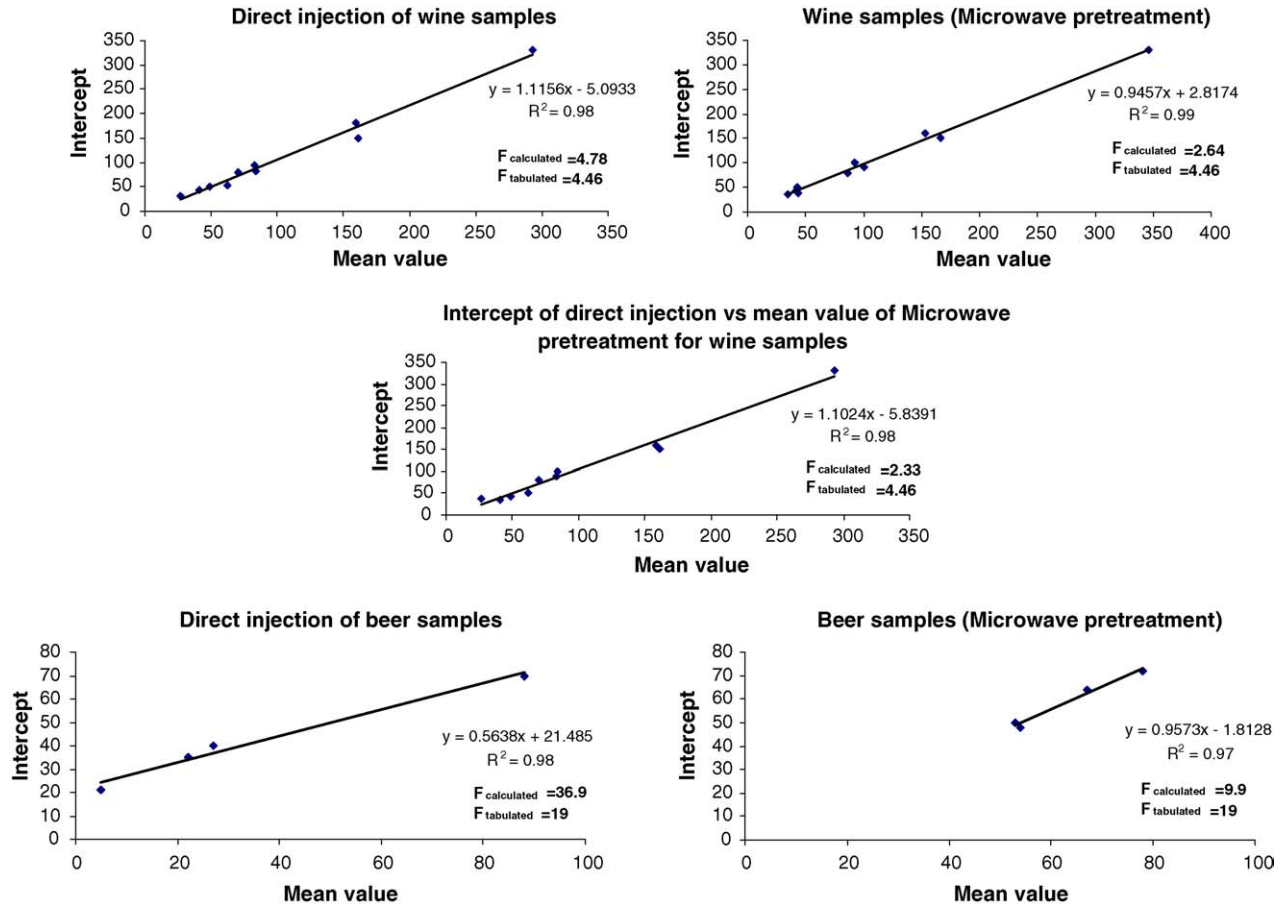

Fig. 4. Statistical study of results for a confidence level of 95%.

Table 3
Results obtained for Cu in beer samples

Sample	Direct injection		Pretreatment	
	Intercept (μg/l)	Mean concentration (μg/l)	Intercept	Mean concentration
Amstel Aguila	27	40 ± 10	54	48 ± 7
German malt dark beer (Steinburg)	22	35 ± 8	53	50 ± 10
German malt beer type bock (Steinburg)	88	70 ± 12	78	72 ± 5
German wheat thick beer (Steinburg)	5	21 ± 15	67	64 ± 12

(12) is statistically equal to zero and then, it can be conclude that determination of copper in beer after the proposed pre-treatment is free of bias errors.

Acknowledgment

The authors thank the Ministerio de Ciencia y Tecnología for financial support (project BQU2002-00527).

References

[1] E.A. Hernandez-Caraballo, R.M. Avila-Gomez, T. Capote, F. Rivas, A.G. Perez, Talanta 60 (6) (2003) 1259–1267.
[2] A.C. Clark, G.R. Scollary, Anal. Chim. Acta 413 (2000) 25–32.
[3] M. Aceto, O. Abollino, M.C. Bruzzoniti, E. Mentasti, C. Sarzanini, M. Melandrino, Food. Addit. Contam. 19 (2) (2002) 126–133.
[4] M.A. Baldo, C. Bragato, S. Daniel, Analyst 122 (1997) 1–5.
[5] A.M. Green, A.C. Clark, G.R. Scollary, Fresenius J. Anal. Chem. 358 (1997) 711–717.
[6] P. Ostapczuk, H.R. Eschnauer, G.R. Scollary, Fresenius J. Anal. Chem. 358 (1997) 723–727.
[7] C.M.R. Almeida, M.T.S.D. Vasconcelos, M. Barbaste, B. Medina, Anal. Bioanal. Chem. 374 (2) (2002) 314–322.
[8] C.M.R. Almeida, M.T.S.D. Vasconcelos, Anal. Chim. Acta 463 (2002) 165–175.
[9] M.M. Castiñeira, R. Brandt, A. von-Bohlen, Fresenius J. Anal. Chem. 370 (5) (2001) 553–558.
[10] J.S. Bian, F. Shan, Y.Q. Li, Guangpuxue Yu Guangpu Fenxi 20 (3) (2000) 381–384.
[11] A. Escobal, C. Iriondo, C. Laborra, E. Ulibarrena, At. Spectrosc. 16 (4) (1995) 162–164.
[12] A.A. Almeida, M.I. Cardoso, J.L.F.C. Lima, At. Spectrosc. 15 (2) (1994) 73–77.
[13] R. Svendsen, W. Lund, Analyst 125 (11) (2000) 1933–1937.

[14] N. Ibáñez, A. Navarro, R. Montoro, J. Inst. Brew. 95 (4) (1989) 257–262.
[15] J. Jaganathan, S.M. Dugar, At. Spectrosc. 18 (5) (1997) 156–159.
[16] D. Bellido-Milla, J.M. Moreno-Perez, M.P. Hernández-Artiga, Spectrochim. Acta B 55 (2000) 855–864.
[17] B. Wyrzkowska, K. Szymczyk, H. Ichichashi, J. Falandysz, B. Skwarzec, S. Yamasaki, J. Agric. Food Chem. 49 (7) (2001) 3425–3431.
[18] P. Viñas, N. Aguinaga, I. Lopez-Garcia, M. Hernandez-Cordoba, J. AOAC Int. 85 (3) (2002) 736–743.
[19] C. Agra-Gutierrez, J.L. Hardcastle, J.C. Ball, R.G. Compton, Analyst 124 (7) (1999) 1053–1057.
[20] M. Llobat-Estelles, R. Marín-Sáez, M.D. San-Martin-Ciges, Fresenius J. Anal. Chem. 342 (7) (1992) 538–546.
[21] M. Llobat-Estelles, C. Alvarez-Alonso, A.R. Maurí-Aucejo, Analusis 21 (4) (1993) 201–206.
[22] A.R. Maurí-Aucejo, M. Llobat-Estelles, R. Marín–Sáez, M.D. San-Martin-Ciges, C. Alvarez-Alonso, Fresenius J. Anal. Chem. 346 (1993) 888–895.
[23] M. Llobat-Estelles, A.R. Maurí-Aucejo, R. Marín–Sáez, M.D. San-Martin-Ciges, A. Cerdán-Vidal, Anal. Chim. Acta 282 (2) (1993) 671–677.
[24] A. Cerdán-Vidal, A.R. Maurí-Aucejo, M. Llobat-Estellés, C. Pascual-Martí, J. Simeón-Martí, Fresenius J. Anal. Chem. 350 (1994) 706–711.
[25] A. Cerdán-Vidal, A.R. Maurí-Aucejo, C. Pascual-Martí, M. Llobat-Estellés, Microchem J. 64 (2000) 201–205.
[26] A. Cerdán-Vidal, M. Llobat-Estellés, A.R. Maurí-Aucejo, C. Pascual-Martí, Anal. Lett. 33 (9) (2000) 1827–1842.
[27] O. Pastor-Ferrer, A.R. Maurí-Aucejo, M. Llobat-Estellés, Fresenius J. Anal. Chem. 367 (2000) 485–490.
[28] A.R. Maurí-Aucejo, M. Llobat-Estellés, R. Marín-Sáez, Anal. Bioanal. Chem. 375 (2003) 643–652.
[29] B.V. L'vov, Spectrochim. Acta 17 (1961) 761–770.
[30] B.V. L'vov, Spectrochim. Acta 33B (1978) 153–193.
[31] W.B. Barnett, M.M. Cooksey, At. Absorpt. Newslett. 18 (3) (1979) 61–65.
[32] J.M. Harnly, J. Anal. Atom. Spectrom. 3 (1988) 43–51.
[33] W. Wegscheider, et al., Chem. Intell. Lab. Sys. 7 (1990) 281–293.
[34] D.A. Sadler, P.R. Boulo, J.S. Soraghan, D. Littlejohn, Spectrochim. Acta 53B (1998) 821–835.
[35] A.R. Maurí-Aucejo, M. Llobat-Estelles, D. Adriá-Cerezo, Anal. Chim. Acta 426 (2001) 135–146.
[36] D.L. Massart, et al., in: B.G.M. Vandeginste, S.C. Rutan (Eds.), Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, 1997, pp. 193–194 (Chapter 8).