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PROFICIENCY TEST ON FTIR WINE ANALYSIS*

TESTE DE DESEMPENHO EM ANÁLISE DE VINHOS POR FTIR

J. L. Moreira[1,2], A. M. Marcos[1], P. Barros[1,2]

[1] Instituto da Vinha e do Vinho, Laboratório Vitivinícola, Unidade Laboratorial de Gaia, Rua Serpa Pinto, 571, 2.º, 4400-307 Vila Nova de Gaia, Portugal. E-mail: ulgaia@ivv.min-agricultura.pt

[2] ALABE – Associação dos Laboratórios de Enologia, Rua Ferreira Borges, 27, 4050–253 Porto, Portugal. E-mail: alabe@net.sapo.pt

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SUMMARY

The FTIR (Fourier Transform Infrared) technology has recently become one of the greatest improvements in the routine work of a wine analysis laboratory.

In Portugal a workgroup of laboratories equipped with FTIR wine analysers has been created in order to optimise this methodology. One of the most important tasks of this workgroup was to carry out a proficiency test for FTIR analysers. This test consisted in the analysis of the same sample by all the participants, using a FTIR wine analyser provided with the same analytical calibration and using the same procedure.

The results obtained presented good reproducibility in what the most relevant parameters are concerned.

This proficiency test enables a more effective quality control of the FTIR results of each laboratory and became an important tool to detect several malfunctions in the equipments of the participants.

Keywords: wine, FTIR, spectrometry, proficiency test, analysis

Palavras-chave: vinho, espetrometria, FTIR, teste de desempenho, análise

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INTRODUCTION

The application of FTIR to wine automatic analysers is an emergent and very promising methodology. It provides excellent results concerning precision for almost all the parameters. Validation parameters such as precision and exactness were obtained in a previous study. Good results of reproducibility for several parameters have been obtained using this equipment (Moreira *et al.*, 2002).

Compared with conventional techniques such as HPLC, FTIR greatly increases the speed of analysis, the main inconvenience being diminished accuracy of results, whereas precision is about the same (Patz *et al.*, 2000).

A workgroup in Portugal was created with the aim of developing wine analysis with the FTIR methodology. Some of the initiatives of this group were the interchange of experience with recent FTIR equipment and the creation of a global wine calibration using samples from several regions of Portugal.

One of the main tasks of this group was the constitution of a proficiency test to evaluate the capability of the equipment to obtain results with good reproducibility. The test became an effective tool to detect malfunctions and other deviations to its normal work.

In this test, a homogeneous wine sample was distributed every month to each participant laboratory with a rigorous procedure of sample preparation and FTIR analysis. Each participant analysed the sample in the corresponding month, using the same calibration and using the same analytical procedure.

MATERIAL AND METHODS

Sample Scheduling

This test started in November 2001 with 6 laboratories equipped with FTIR wine analysers, having the number of laboratories increased to 9 until July 2002.

Each monthly wine sample (9 months - 1 sample per month) was divided into 0.75 L aliquots. No specific date for the analysis was defined; that decision was left to for the participants. This was not self-defeating and it approached the execution of the tests to the real situation in the laboratories. All the wines analysed were dry (less than 5 g/L of total sugars), 6 being red and 3 white.

Sample preparation

The wine for each monthly test was homogenised, bottled in the sufficient amount of 0.75 L aliquots for all the participants and rapidly distributed. This procedure was carried out by each participant in rotation. No other sample treatment has been executed prior to analysis.

Equipment

All the laboratories were equipped with a FOSS Winescan FT-120 FTIR wine spectrometer using PLS (Partial Least Squares) algorithm to calculate the results. The analytical procedure was described by Moreira *et al.* (2002).

Analysis

All the samples were analysed in duplicate concerning all the parameters scheduled in the corresponding month, using the calibration previously developed by the same workgroup (Moreira *et al.*, 2002), which was electronically provided to all the members and installed in each equipment.

The calibration distributed (PLS coefficients) allowed the analysis of 19 parameters: Density, Ethanol, Dry extract, Total sugars, Total acid, Volatile acid, Total SO_2, pH, Total polyphenol index, Ash, Conductivity, Glucose, Fructose, Glycerol, Citric acid, Tartaric acid, Malic acid, Lactic acid and Sulphates.

Statistical analysis

The statistical analysis of the results was made by an independent participant who was in charge of treating and distributing the results. Once we are not facing trace analytical results, a quantification limit was not performed in this work.

The Grubbs test was applied to single and double outliers, after eliminating non-sense negative values due to PLS algorithm. If the test was less than the critical value at 5%, the item was accepted. If the test lied between the critical values at 5% and 1%, it was considered a straggler. If the test was greater than the critical value at 1%, it was considered a statistical outlier (ISO 5725-2, 1994).

Average results (x), between laboratory standard deviation (s_L), reproducibility standard deviation (s_R) and reproducibility (R) were calculated by, including straggler and rejecting outliers.

Repeatability (r) results were considered constant and determined by a single laboratory using 114 samples analysed in duplicate (Table I).

TABLE I

Repeatability results
Resultados de repetibilidade

Laboratory	Density (g/cm^3)	Ethanol (% vol.)	Dry extract (g/dm^3)	Total sugars (g/dm^3)	Total acid (g/dm^3)	Volatile acid (g/dm^3)	Total SO_2 (mg/dm^3)	pH	Total polyphenol index	Ash (g/dm^3)	Conductivity ($mS\ cm^{-1}$)	Glucose (g/dm^3)	Fructose g/dm^3)	Glycerol (g/dm^3)	Citric acid (g/dm^3)	Tartaric acid (g/dm^3)	Malic acid (g/dm^3)	Lactic acid (g/dm^3)	Sulphates (g/dm^3)
r	0.00016	0.034	0.271	0.195	0.057	0.027	7.491	0.024	1.179	0.092	0.040	0.424	0.152	1.357	0.033	0.086	0.086	0.111	0.031

RESULTS AND DISCUSSION

The results obtained by the workgroup from November 2001 to July 2002 are presented in Table II to X. The names of the laboratories were coded (A to I) for confidentiality purposes.

TABLE II

Results in November/2001
Resultados em Novembro de 2001

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9920	12.29	26.20	2.30	5.90	0.43	63	3.45	47.8						0.55				
B	0.9921	12.27	26.40	2.50	5.60	0.43	56	3.44	49.0						0.38				
C	0.9919	12.30	26.60	2.50	5.70	0.34	74	3.42	44.6						0.45				
D	0.9919	12.33	26.10	2.30	5.90	0.40	42	3.44	45.8						0.45				
E	0.9921	12.28	26.80	2.40	5.70	0.35	55	3.41	45.1						0.57				
F	0.9921	12.29	26.20	2.40	5.70	0.41	62	3.44	46.4						0.43				
G																			
H																			
I																			
$\bar{X}$	0.9920	12.29	26.38	2.40	5.75	0.39	59	3.43	46.5						0.47				
s_L	0.00009	0.019	0.263	0.075	0.122	0.039	10.5	0.014	1.65						0.073				
s_R	0.00011	0.022	0.280	0.102	0.123	0.040	10.8	0.016	1.70						0.074				
R	**0.00030**	**0.063**	**0.784**	**0.286**	**0.345**	**0.112**	**30.3**	**0.045**	**4.76**						**0.206**				

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE III

Results in December/2001
Resultados em Dezembro de 2001

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9926	13.29	29.90	4.55	5.65	0.70	79	3.51	59.1						0.38				
B	0.9924	13.36	29.40	4.55	5.55	0.70	62	3.51	57.7						0.36				
C	0.9924	~~13.90~~	~~31.50~~	4.90	5.80	0.72	72	3.47	59.1						0.42				
D	0.9926	13.31	29.80	4.70	5.30	0.67	73	3.49	60.3						0.31				
E	0.9924	13.39	29.60	4.60	5.40	0.67	56	3.50	58.8						0.32				
F	0.9926	13.35	29.80	4.60	5.50	0.70	70	3.51	58.1						0.36				
G																			
H																			
I																			
$\bar{X}$	0.9925	13.34	29.70	4.65	5.53	0.69	69	3.50	58.8						0.36				
s_L	0.00010	0.039	0.188	0.125	0.177	0.018	8.1	0.015	0.88						0.039				
s_R	0.00012	0.041	0.211	0.143	0.179	0.021	8.5	0.017	0.98						0.041				
R	**0.00033**	**0.115**	**0.592**	**0.400**	**0.500**	**0.058**	**23.9**	**0.048**	**2.74**						**0.115**				

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE IV

Results in January/2002
Resultados em Janeiro de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9927	12.56	28.70	2.40	5.69	0.45	80	3.56	52.4						0.49				
B	0.9927	12.52	28.60	2.70	5.30	0.42	80	3.56	53.8						0.42				
C	0.9927	12.51	28.70	2.50	5.40	0.43	84	3.55	52.3						0.39				
D	0.9926	12.59	~~28.05~~	2.42	5.62	0.46	71	3.57	49.9						0.55				
E	0.9927	12.50	28.60	2.40	5.50	0.41	76	3.56	52.1						0.40				
F	0.9928	12.54	28.70	2.60	5.50	0.45	76	3.56	50.7						0.44				
G																			
H																			
I																			
$\bar{X}$	0.9927	12.54	28.66	2.50	5.50	0.44	78	3.56	51.9						0.45				
s_L	0.00005	0.033	0.000	0.113	0.141	0.018	4.1	0.002	1.34						0.061				
s_R	0.00007	0.035	0.097	0.133	0.142	0.021	4.9	0.009	1.40						0.062				
R	**0.00021**	**0.098**	**0.271**	**0.372**	**0.399**	**0.058**	**13.8**	**0.024**	**3.93**						**0.174**				

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE V

Results in February/2002
Resultados em Fevereiro de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9927	12.37	27.30	2.46	4.98	0.46	65	3.60	54.2						0.15				
B	0.9926	12.39	27.20	2.70	4.60	0.43	70	3.58	54.0						0.10				
C	0.9925	12.39	27.30	2.40	4.80	0.40	64	3.61	55.4						0.12				
D	0.9924	12.50	27.08	2.43	4.99	0.46	54	3.58	52.7						0.12				
E	0.9924	12.40	26.70	2.40	4.70	0.49	69	3.60	53.0						0.08				
F	0.9926	12.43	27.20	2.50	4.80	0.44	47	3.61	54.8						0.12				
G																			
H																			
I																			
$\bar{X}$	0.9925	12.41	27.13	2.48	4.81	0.45	61	3.60	54.0						0.11				
s_L	0.00011	0.046	0.215	0.102	0.153	0.030	8.9	0.012	0.97						0.021				
s_R	0.00013	0.048	0.236	0.124	0.154	0.032	9.3	0.015	1.06						0.024				
R	**0.00036**	**0.133**	**0.661**	**0.347**	**0.431**	**0.088**	**26.1**	**0.042**	**2.97**						**0.067**				

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE VI

Results in March/2002
Resultados em Março de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9944	12.66	32.60	3.79	5.98	0.54	105	3.51	51.3						0.31				
B	0.9944	12.72	32.70	4.10	5.70	0.49	101	3.48	51.6						0.27				
C	0.9944	12.71	33.00	3.90	6.00	0.44	103	3.49	53.3						0.28				
D	0.9943	12.83	32.77	3.83	6.06	0.51	97	3.53	51.5						0.34				
E	0.9942	12.80	32.40	3.90	5.90	0.54	98	3.52	51.7						0.34				
F	0.9945	12.80	33.20	3.90	5.90	0.49	97	3.52	52.7						0.35				
G																			
H																			
I																			
$\bar{X}$	0.9944	12.75	32.78	3.90	5.92	0.50	100	3.51	52.0						0.32				
s_L	0.00010	0.066	0.277	0.095	0.125	0.037	2.8	0.018	0.72						0.036				
s_R	0.00011	0.067	0.294	0.118	0.126	0.038	3.9	0.020	0.83						0.038				
R	**0.00031**	**0.187**	**0.822**	**0.329**	**0.354**	**0.107**	**10.8**	**0.057**	**2.33**						**0.106**				

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE VII

Results in April/2002
Resultados em Abril de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9907	12.24	22.10	1.64	6.11	0.25	95	3.24		2.27	1.76	1.02	0.76	3.01	0.31	2.40	2.12	0.01	0.480
B	0.9908	12.26	22.00	1.76	5.74	0.20	93	3.19		2.16	1.68	0.08	0.82	2.68	0.26	1.80	1.97		0.643
C	0.9906	12.26	21.90	1.50	6.17	0.16	84	3.20		2.06	1.77	0.43	0.45	2.26	0.29	2.24	2.09	0.04	0.556
D	0.9906	12.29	21.70	1.60	6.08	0.23	90	3.22		2.30	1.77	0.32	0.52	3.09	0.28	2.27	1.96	0.09	0.544
E	0.9907	12.39	22.20	1.38	6.09	0.25	87	3.28		2.46	1.90		0.83	2.36	0.28	1.84	2.06	0.21	0.627
F	0.9907	12.38	21.90	1.51	5.99	0.19	93	3.21		2.34	1.67	0.53	0.87	3.71	0.27	2.21	1.92	0.06	0.575
G																			
H																			
I																			
$\bar{X}$	0.9907	12.30	21.97	1.57	6.03	0.21	90	3.22		2.27	1.76	0.48	0.71	2.85	0.28	2.13	2.02	0.08	0.571
s_L	0.00006	0.065	0.161	0.122	0.153	0.035	3.7	0.032		0.138	0.082	0.330	0.174	0.413	0.015	0.246	0.078	0.072	0.059
s_R	0.00009	0.066	0.188	0.140	0.154	0.037	4.6	0.033		0.142	0.083	0.363	0.182	0.637	0.019	0.248	0.084	0.082	0.060
R	**0.00024**	**0.184**	**0.526**	**0.393**	**0.432**	**0.103**	**12.8**	**0.092**		**0.397**	**0.234**	**1.017**	**0.510**	**1.783**	**0.053**	**0.693**	**0.234**	**0.230**	**0.167**

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE VIII

Results in May/2002

Resultados em Maio de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9931	12.14	27.90	2.94	4.83	0.71	91	3.54	40.1	3.03	2.02	1.07	1.05	6.68	0.09	0.80		1.25	0.677
B	0.9933	12.15	28.00	3.12	4.51	0.62	96	3.46	36.6	2.82	2.03	0.19	1.07	7.56		0.39		1.19	0.835
C	0.9930	12.18	27.70	2.97	4.80	0.62	87	3.50	39.0	2.78	2.07	0.74	0.77	6.10	0.06	0.77		1.10	0.721
D	0.9929	12.20	27.20	2.54	4.86	0.67	85	3.53	41.4	3.15	2.02	0.17	0.77	6.42	0.06	0.68		1.38	0.721
E	0.9928	12.16	27.20	2.83	4.64	0.62	72	3.46	39.2	3.02	2.01		0.85	6.45	0.02	0.40		1.37	0.848
F	0.9930	12.28	27.80	2.88	4.84	0.62	76	3.49	39.7	2.94	1.91	0.70	1.18	7.26	0.03	0.70		1.37	0.756
G	0.9929	12.10	27.40	2.87	5.11	0.74	100	3.52	43.3	3.18	2.00	1.02	0.69	5.96	0.08	0.99		1.30	0.704
H																			
I																			
$\bar{X}$	0.9930	12.17	27.60	2.88	4.80	0.66	87	3.50	39.9	2.99	2.01	0.65	0.91	6.63	0.06	0.68		1.28	0.752
s_L	0.00016	0.056	0.325	0.170	0.187	0.050	9.9	0.033	2.06	0.151	0.048	0.376	0.183	0.477	0.026	0.215		0.103	0.065
s_R	0.00017	0.057	0.339	0.184	0.188	0.051	10.3	0.034	2.11	0.154	0.050	0.406	0.191	0.680	0.029	0.218		0.110	0.066
R	**0.00047**	**0.161**	**0.948**	**0.514**	**0.528**	**0.143**	**28.8**	**0.094**	**5.90**	**0.432**	**0.140**	**1.136**	**0.534**	**1.904**	**0.080**	**0.609**		**0.308**	**0.186**

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)

2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE IX

Results in June/2002

Resultados em Junho de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9890	12.55	19.10	2.15	5.20	0.39	117	3.08		1.88	1.48	1.02	0.86	2.93	0.18	1.63	1.60		0.684
B	~~0.9896~~	12.44	19.10	~~2.94~~	~~4.30~~	0.25	98	2.93		1.74	1.35	0.07	~~2.29~~		0.08	~~0.77~~	~~0.54~~	~~0.69~~	~~1.043~~
C	0.9889	12.59	18.80	2.19	5.17	0.35	119	3.04		1.72	1.53	0.51	0.42	2.43	0.16	1.65	1.66		0.721
D	0.9889	12.62	18.73	2.08	5.24	0.38	121	3.07		1.96	1.44	0.65	0.75	2.83	0.14	1.59	1.44	0.12	0.730
E	0.9888	12.60	18.50	1.99	5.02	0.31	108	3.00		1.84	1.45		0.66	2.94	0.12	~~1.14~~	1.44	0.07	~~0.867~~
F	0.9889	12.71	19.00	1.95	5.22	0.30	116	3.00		1.84	1.35	0.76	0.82	3.95	0.14	1.56	1.41	0.03	0.752
G	0.9888	12.57	18.90	1.95	5.32	0.37	114	3.08		2.02	1.43	0.97	0.47	3.50	0.16	1.72	1.58		0.678
H	0.9889	12.68	18.90	1.86	5.25	0.37	124	3.06		1.94	1.44	0.02	0.47	2.76	0.11	1.42	1.34	0.20	0.788
I	0.9890	12.52	19.10	2.04	5.29	0.38	118	3.08		1.90	1.49	0.39	0.34	3.25	0.15	1.69	1.63		0.718
$\bar{X}$	0.9889	12.59	18.90	2.03	5.21	0.34	115	3.04		1.87	1.44	0.55	0.60	3.07	0.14	1.61	1.51	0.22	0.724
s_L	0.00007	0.081	0.191	0.099	0.091	0.047	7.5	0.051		0.096	0.059	0.361	0.195	0.331	0.029	0.097	0.117	0.268	0.037
s_R	0.00009	0.082	0.214	0.121	0.093	0.048	8.0	0.052		0.101	0.061	0.391	0.202	0.587	0.031	0.102	0.121	0.271	0.039
R	**0.00024**	**0.229**	**0.599**	**0.339**	**0.260**	**0.134**	**22.4**	**0.146**		**0.283**	**0.170**	**1.095**	**0.566**	**1.644**	**0.088**	**0.285**	**0.338**	**0.758**	**0.109**

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)

2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

TABLE X

Results in July/2002
Resultados em Julho de 2002

Laboratory	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
A	0.9884	12.75	18.00	1.76	5.04	0.32	80	3.18		1.88	1.39	0.60	0.84	1.50	0.28	1.84	1.76	0.00	0.387
B	0.9886	12.77	18.30	1.57	4.92	0.30	77	3.21		2.01	1.38	0.23	1.08	2.57	0.18	1.43	1.40	0.20	0.560
C	0.9885	12.78	18.20	1.70	4.97	0.29	85	3.17		1.87	1.47	0.28	0.78	2.08	0.22	1.64	1.71		0.515
D	0.9882	12.88	17.58	1.58	5.05	0.30	81	3.18		1.95	1.37	0.16	0.75	1.71	0.23	1.66	1.55	0.21	0.450
E	0.9882	12.80	17.60	1.50	4.82	0.24	67	3.12		1.86	1.39		0.75	1.23	0.20	1.23	1.54	0.23	0.618
F	0.9883	12.89	17.90	1.60	5.01	0.24	73	3.12		1.89	1.28	0.10	0.85	2.30	0.23	1.70	1.56	0.12	0.490
G	0.9884	12.79	18.10	1.59	5.14	0.27	78	3.19		1.99	1.37	0.72	0.59	2.39	0.22	1.77	1.65	0.07	0.435
H	0.9884	12.82	17.90	1.36	5.04	0.29	81	3.18		1.95	1.36		0.60	1.51	0.19	1.53	1.43	0.28	0.539
I	0.9884	12.74	18.00	1.48	5.07	0.30	80	3.18		1.84	1.35		0.29	2.88	0.20	1.77	1.72	0.04	0.425
$\bar{X}$	0.9884	12.80	17.95	1.57	5.01	0.28	78	3.17		1.92	1.37	0.13	0.73	2.02	0.22	1.62	1.59	0.14	0.491
s_L	0.00012	0.052	0.234	0.107	0.092	0.027	4.9	0.031		0.056	0.048	0.228	0.215	0.443	0.028	0.192	0.126	0.097	0.074
s_R	0.00013	0.054	0.254	0.128	0.094	0.029	5.6	0.032		0.065	0.050	0.274	0.222	0.657	0.031	0.194	0.130	0.105	0.074
R	**0.00038**	**0.150**	**0.710**	**0.358**	**0.264**	**0.080**	**15.6**	**0.090**		**0.182**	**0.141**	**0.766**	**0.621**	**1.839**	**0.086**	**0.544**	**0.363**	**0.293**	**0.208**

1) Grubbs test statistic between critical value at 5% and l%: straggler (underline)
2) Grubbs test statistic greater than critical value at l%: ~~outlier~~ (strikethrough)

The average reproducibility was then calculated for the testing period (Table XI).

TABLE XI

Average Reproducibility during the testing period
Reprodutibilidade média durante o período de teste

Month	Density (g/cm³)	Ethanol (% vol.)	Dry extract (g/dm³)	Total sugars (g/dm³)	Total acid (g/dm³)	Volatile acid (g/dm³)	Total SO_2 (mg/dm³)	pH	Total polyphenol index	Ash (g/dm³)	Conductivity (mS cm⁻¹)	Glucose (g/dm³)	Fructose g/dm³)	Glycerol (g/dm³)	Citric acid (g/dm³)	Tartaric acid (g/dm³)	Malic acid (g/dm³)	Lactic acid (g/dm³)	Sulphates (g/dm³)
Nov 2001	0,00030	0,063	0,784	0,286	0,345	0,112	30,3	0,045	4,76						0,206				
Dec 2001	0,00033	0,115	0,592	0,400	0,500	0,058	23,9	0,048	2,74						0,115				
Jan 2002	0,00021	0,098	0,271	0,372	0,399	0,058	13,8	0,024	3,93						0,174				
Feb 2002	0,00036	0,133	0,661	0,347	0,431	0,088	26,1	0,042	2,97						0,067				
Mar 2002	0,00031	0,187	0,822	0,329	0,354	0,107	10,8	0,057	2,33						0,106				
Apr 2002	0,00024	0,184	0,526	0,393	0,432	0,103	12,8	0,092		0,397	0,234	1,017	0,510	1,783	0,053	0,693	0,234	0,230	0,167
May 2002	0,00047	0,161	0,948	0,514	0,528	0,143	28,8	0,094	5,90	0,432	0,140	1,136	0,534	1,904	0,080	0,609		0,308	0,186
Jun 2002	0,00024	0,229	0,599	0,339	0,260	0,134	22,4	0,146		0,283	0,170	1,095	0,566	1,644	0,088	0,285	0,338	0,758	0,109
Jul 2002	0,00038	0,150	0,710	0,358	0,264	0,080	15,6	0,090		0,182	0,141	0,766	0,621	1,839	0,086	0,544	0,363	0,293	0,208
R (Average)	0,00031	0,147	0,657	0,371	0,390	0,098	20,5	0,071	3,77	0,324	0,171	1,004	0,558	1,793	0,108	0,533	0,312	0,397	0,168
R (Official methods)*	0.00037	0.19	-	-	0.4	0.08	15	-	-	-	-	-	-	-	-	-	-	-	0.051

* - (E.C. Regulation. 1990)

The Grubbs test allowed the detection of several outliers and stragglers. Some of the outliers could be explained by a major malfunction of the equipment (Table VII – Laboratory B), causing a considerable deviation to the test average. The remaining outliers do not inspire much concern once no laboratories presented outliers repeatedly in the same parameter. These outliers are probably the result of a normal drift in such sensitive equipment as a FTIR analyser.

The following graphics (Fig. 1 to Fig. 8) represent the evolution of the results along the testing period and the overall average Reproducibility obtained for 8 of the most relevant parameters analysed.

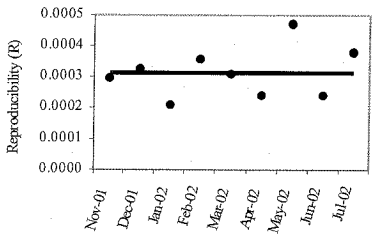

Fig. 1 – Reproducibility (•) and Average (—) for Density.

Reprodutibilidade (•) e Média (—) para a Massa volúmica.

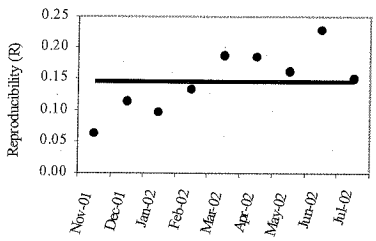

Fig. 2 – Reproducibility (•) and Average (—) for Ethanol.

Reprodutibilidade (•) e Média (—) para o Titulo alcoométrico volúmico.

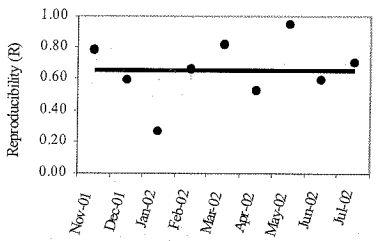

Fig. 3 – Reproducibility (•) and Average (—) for Dry extract.

Reprodutibilidade (•) e Média (—) para o Extracto seco total.

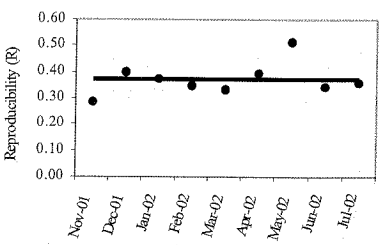

Fig. 4 – Reproducibility (•) and Average (—) for Total sugars.

Reprodutibilidade (•) e Média (—) para os Açúcares totais.

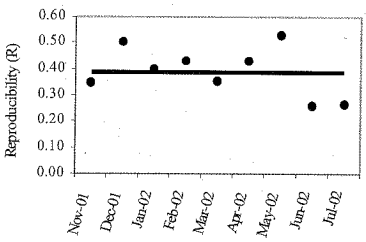

Fig. 5 – Reproducibility (•) and Average (—) for Total acid.

Reprodutibilidade (•) e Média (—) para a Acidez total.

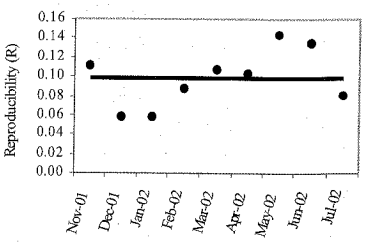

Fig. 6 – Reproducibility (•) and Average (—) for Volatile acid.

Reprodutibilidade (•) e Média (—) para a Acidez volátil.

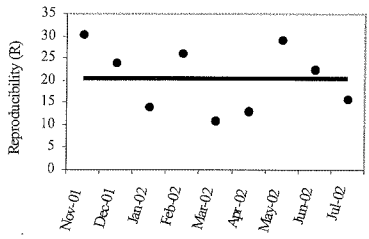

Fig. 7 – Reproducibility (•) and Average (—) for Total SO_2.

Reprodutibilidade (•) e Média (—) para o SO_2 Total.

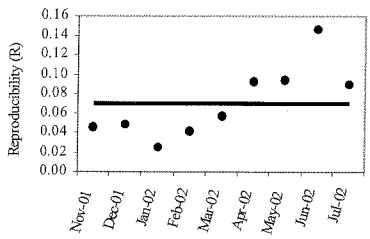

Fig. 8 – Reproducibility (•) and Average (—) for pH.

Reprodutibilidade (•) e Média (—) para o pH.

The results in June 2002 were exceptionally poor (for the first time two laboratories had outliers results in the same month) possibly due to a misuse of the equipments.

The aliquots were considered sufficiently homogeneous by the application of the preparation procedure, although not confirmed by an exhaustive test.

CONCLUSIONS

In this test proficiency test very good reproducibility results were achieved for the most relevant parameters. Reproducibility results were lower than those of the European Official Methods for density, ethanol and total acid but slightly higher for volatile acid, total SO_2 and sulphates. The reproducibility (R) results are adequate to routine work in a wine analysis laboratory.

According to results that were not presented the usage an "equalizer liquid" (a commercial standard material for the absorvance and frequency adjustment of the equipment) allows the achievement of a negligible improvement in the R results for almost all parameters.

The proficiency test also allowed a very strict quality control of routine wine analysis. With this aim monthly control charts were created and a statistical analysis was made in order to detect any significant deviation to the average results.

AKNOWLEDGEMENTS

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RESUMO

Teste de desempenho em análise de vinhos por FTIR

A Espectroscopia de Infravermelho com Transformada de Fourier (FTIR) tornou-se recentemente uma das maiores inovações na análise de rotina de um laboratório de enologia.

Em Portugal foi criado um grupo de laboratórios com equipamentos analisadores de vinho por FTIR, com o objectivo de optimizar esta metodologia. Uma das mais importantes tarefas deste grupo foi levar a cabo um teste de desempenho para analisadores FTIR. Este teste consistiu na análise, por todos os participantes, da mesma amostra, usando um analisador de vinho por FTIR equipado com a mesma calibração analítica e usando o mesmo procedimento.

Os resultados obtidos apresentam boa reprodutibilidade para os parâmetros mais relevantes.

Este teste de desempenho possibilita um controlo de qualidade mais eficiente dos resultados dos equipamentos FTIR de cada laboratório e tornou-se uma importante ferramenta na detecção de diversas situações de funcionamento deficiente dos equipamentos.

RÉSUMÉ

Test d'aptitude sur l'analyse de vin par FTIR

La technologie de FTIR (Spectrométrie d'Infrarouge avec Transformée de Fourier) s'est récemment imposée comme l'une des plus grandes améliorations du travail de routine des laboratoires d'oenologie.

Au Portugal, un groupe de laboratoires equipés avec des analyseurs de vin par FTIR a été créé dans le but d'optimiser cette méthodologie. Une des tâches les plus importantes de ce groupe a été de mettre en place un test d'aptitude des analyseurs de vin par FTIR. Ce test a consisté dans l'analyse du même échantillon par tous les participants à travers l'utilisation d'analyseurs de vin par FTIR equipés avec le même calibrage analytique, et en utilisant la même procédure d'analyse.

Les résultats obtenus présentent une bonne reproductibilité en ce qui concerne les paramètres les plus pertinents.

En permettant un contrôle plus efficient de la qualité des résultats provenant des analyseurs de vin par FTIR, ce test d'aptitude est devenu un important outil pour détecter plusieurs défauts de fonctionnement dans les équipements.

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