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COMPARISON OF WINE DENSITY AND ALCOHOLIC STRENGTH MEASUREMENT BY HYDROSTATIC BALANCE AND ELECTRONIC DENSITY-METER

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Key words:
specific gravity (sg)/density (d), alcoholic strength (as), hydrostatic balance (HB), electronic density-meter (ED), methods comparison

Summary: for quality control in enology (Unione Italiana Vini, Verona I)
Data from pluriannual monthly ring tests on wines at different composition, organised with official criteria by an Italian company, have been provided for investigating the repeatability of the specific gravity measurement of wine using hydrostatic balance and electronic density-meter, as well as, after a proper selection of data according to statistical methods, for comparing reproducibility and precision results for specific gravity and alcoholic strength using both methods. For the first aim, we can confirm the previous results on repeatability in one lab; for the second goal, good linear correlations between results from both measurements with a proper distribution of scores have been obtained, as well as reproducibility values that can fit with some available results for reference methods of EC or by OIV already recognised.

Introduction.
Measurement of alcohol content in wine using electronic density-meter has been recently made official by OIV (Resolution OENO 8/2000) and admitted in the Annex A of the Collection of the OIV International Method of Analyses: repeatability in a proper range (between 4-18% Vol), and reproducibility were considered in an inter-laboratory ring test. Besides, both methods referring to hydrostatic balance and electronic density-meter were recognised by EC Reg. n. 2870/2000 as reference methods along with the pycnometry, for the measure of the alcoholic strength of spirits. In the OIV session of March 2001, a Green Paper (F.V. n. 1096; Cabanis *et al.*, 1999) concerning an intra-laboratory comparison of the hydrostatic balance with the pycnometry to measure the alcoholic degree of wines has been presented. In the same session, the results of the intra-laboratory validation of specific gravity measurement obtained by the hydrostatic balance (EC usual method as in Reg. n. 2676/90, being the pycnometry the reference method) in comparison to those by the electronic density-meter have been also submitted by Versini et Larcher (2001). Now, we present a comparison of measurement of wine specific gravity and alcoholic strength achieved with the hydrostatic balance and the electronic density-meter, assuming this latter method as OIV reference method for alcoholic strength determination.

Equipments and samples:
Equipments:
- electronic hydrostatic balance (precision at the 5th decimal) eventually equipped with a data treatment device:
- electronic density-meter (Paar-type) eventually equipped with autosampler.

Samples:
- wines of different density and alcoholic strength monthly prepared on industrial scale, taken from a bottled stock properly stored, and delivered as anonymous products to the laboratories participating into the monthly ring test organised by Unione Italiana Vini (~~Verona, Italy~~) according to ISO 5725 (UNI 9225) rules and 'International Protocol of Proficiency test for chemical analysis laboratories' established by AOAC, ISO and IUPAC (J. AOAC Intern., **1993**, *74/4*) and after guidelines ISO 43 and ILAC G13. An annual report of all tested determinations is supplied by the cited company to all participants.

Results and discussion:
According to some validation method rules as in the OIV project final resolution OENO/SCMA/97/84, on each sample a twice consecutive specific gravity and/or alcoholic strength measurement was carried out by

almost all labs using both methods. Only 3 labs performed all the measurements of specific gravity on several samples using both equipments (Tab. 1).
Results in papers above mentioned proved that the repeatability standard deviation s_r and repeatability r, are comparable for both methods measuring both specific gravity and alcoholic strength. As a further validation test, we considered altogether the data of Table 2 to draw in Fig. 1 the correlation between the two measurements of specific gravity (n. 63 couples of data): r=.99992; sg (HB) = -.00943 + 1.00958 [sg (ED)]. If considering separately as a couple of data the first of one method vs. the first of the other and the second of one vs. the second result by the second, we still obtain very good correlations with the same r's (= .99991 and .99992) and very similar relationships: sg (HB) = -.01033 + 1.01049 [sg (ED)] and sg (HB) = -.00851 + 1.00866 [sg (ED)], respectively. *Sr* and *r* of the two methods are comparable as demonstrated in a previous intra-laboratory test (Versini et Larcher, 20001).
As for a study of reproducibility, mean and standard deviation for each type of measure and sample analysed (n. 27) are reported in Tab. 2. The data distribution in such trial-like test including a rather high number of labs can approximate the real situation of techniques applied by oenologycal companies and control labs in Italy. Quite all samples have been analysed twice and the total number of analyses is listed. Each series of first and second measurement of data supplied by different labs has been submitted to skewness and kurtosis tests after Barnett V. & Lewis T. (*Outliers in statistical data*, 1984, Wiley, Chichester, UK) - preferred to that of Cochrane to evaluate more then one outlier - to eliminate outliers. The much more numerous labs using hydrostatic balance have been reduced considering only those that supplied data from 1996 to 2000 vintage presenting outliers (significance higher than 95%) at less then 3%, and, as for the data of 2000 and 2001, also labs that improved the performance overcoming such selection criteria.
The data in Tab. 2 were submitted to a linearity test both for the mean values of densimetric measurements obtaining a highly significant linear correlation (r=0.99999; sg(HB) = -.0002016 + 1.002036 [sg(ED)]) (Fig. 2), and of the alcoholic strength with a similar very good linear correlation (r=0.99996; as(HB) = .071+ 0.994 [as(ED)]) (Fig. 3), in both cases showing a negligible effect in changing the correlation including or not the sample still as a must for its very low alcoholic strength. For both measurements, optimal parameters for precision and accuracy were obtained.
Plots of scores between each mean value of specific gravity by hydrostatic balance in comparison with that by electronic density-meter, are statistically distributed around zero, with a mean score difference close to the instrument precision for the specific gravity (Fig. 4) or lower for the alcoholic strength measurement (Fig. 5). In these calculations the values referred to the must sample were excluded due to the quite different standard deviation for all the methods in respect to the wine measurements.
The evaluation of the reproducibility standard deviation S_R and reproducibility R - considering the standard deviation of the measurement of each sample as the relevant score of that method for such calculations - indicates similar values for both methods, resulting R in any case lower than the value established by EC Reg. n. 2676/90, i.e. 0.00045 g/cm^3 for the specific gravity for sweet wines and 0.19 % Vol for the alcoholic strength.

Conclusion

The results above discussed proved that ~~the~~ at present most spread density-metric methods, i.e. the hydrostatic balance and the electronic density-meter are comparable as for repeatability and reproducibility parameters, as well as for the accuracy also for values typical of products fitting the wine-category, as it was demonstrated for the spirits in EC regulation n. 2870/2000.

Table 1: Measurements of specific gravity and simple statistics of 62 different monthly samples of wines analysed in 3 laboratories with two equipments.

			Hydrostatic balance				Electronic density-meter			
month	year	laboratory code	first measure	second measure	mean	difference (2nd -1st)	first measure	second measure	mean	difference (2nd -1st)
3	1999	101	0.99370	0.99380	0.99375	0.00010	0.99410	0.99414	0.99412	0.00004
4	1999	101	1.01103	1.01102	1.01103	-0.00001	1.01100	1.01105	1.01103	0.00005
5	1999	101	0.99460	0.99446	0.99453	-0.00014	0.99438	0.99414	0.99426	-0.00024
8	1999	101	0.99226	0.99241	0.99234	0.00015	0.99235	0.99235	0.99235	0.00000
10	1999	101	0.99226	0.99241	0.99234	0.00015	0.99235	0.99235	0.99235	0.00000
11	1999	101	1.01133	1.01133	1.01133	0.00000	1.01111	1.01121	1.01116	0.00010
2	2000	101	0.99231	0.99286	0.99259	0.00055	0.99257	0.99249	0.99253	-0.00008
3	2000	101	1.07392	1.07402	1.07397	0.00010	1.07307	1.07329	1.07318	0.00022
3	1998	24	0.99435	0.99435	0.99435	0.00000	0.99431	0.99431	0.99431	0.00000
6	1998	24	1.01048	1.01048	1.01048	0.00000	1.01048	1.01048	1.01048	0.00000
7	1998	24	0.99241	0.99241	0.99241	0.00000	0.99241	0.99242	0.99242	0.00001
9	1998	24	1.01290	1.01290	1.01290	0.00000	1.01288	1.01288	1.01288	0.00000
10	1998	24	0.99342	0.99342	0.99342	0.00000	0.99332	0.99332	0.99332	0.00000
12	1998	24	1.01019	1.01019	1.01019	0.00000	1.01018	1.01018	1.01018	0.00000
1	1999	24	0.99351	0.99351	0.99351	0.00000	0.99351	0.99351	0.99351	0.00000
3	1999	24	0.99365	0.99365	0.99365	0.00000	0.99361	0.99361	0.99361	0.00000
4	1999	24	1.01110	1.01110	1.01110	0.00000	1.01108	1.01108	1.01108	0.00000
5	1999	24	0.99446	0.99446	0.99446	0.00000	0.99446	0.99446	0.99446	0.00000
6	1999	24	0.99231	0.99231	0.99231	0.00000	0.99231	0.99231	0.99231	0.00000
7	1999	24	1.01000	1.01000	1.01000	0.00000	1.00998	1.00998	1.00998	0.00000
8	1999	24	0.99241	0.99241	0.99241	0.00000	0.99241	0.99242	0.99242	0.00001
9	1999	24	0.99381	0.99381	0.99381	0.00000	0.99381	0.99381	0.99381	0.00000
10	1999	24	0.99241	0.99241	0.99241	0.00000	0.99241	0.99242	0.99242	0.00001
1	2000	24	0.99372	0.99372	0.99372	0.00000	0.99371	0.99371	0.99371	0.00000
1	1996	67	1.01158	1.01158	1.01158	0.00000	1.01124	1.01121	1.01123	-0.00003
2	1996	67	0.99481	0.99481	0.99481	0.00000	0.99483	0.99490	0.99487	0.00007
3	1996	67	0.99301	0.99301	0.99301	0.00000	0.99275	0.99284	0.99280	0.00009
4	1996	67	0.99341	0.99341	0.99341	0.00000	0.99341	0.99342	0.99342	0.00001
5	1996	67	1.07840	1.07840	1.07840	0.00000	1.07758	1.07774	1.07766	0.00016
9	1996	67	0.99311	0.99321	0.99316	0.00010	0.99328	0.99340	0.99334	0.00012
11	1996	67	1.01208	1.01208	1.01208	0.00000	1.01138	1.01136	1.01137	-0.00002
12	1996	67	0.99251	0.99251	0.99251	0.00000	0.99245	0.99241	0.99243	-0.00004
1	1997	67	0.99271	0.99271	0.99271	0.00000	0.99273	0.99263	0.99268	-0.00010
2	1997	67	0.99281	0.99281	0.99281	0.00000	0.99270	0.99270	0.99270	0.00000
3	1997	67	0.99331	0.99341	0.99336	0.00010	0.99348	0.99370	0.99359	0.00022
4	1997	67	1.01148	1.01148	1.01148	0.00000	1.01121	1.01121	1.01121	0.00000
5	1997	67	0.99271	0.99271	0.99271	0.00000	0.99272	0.99272	0.99272	0.00000
6	1997	67	1.01078	1.01078	1.01078	0.00000	1.01035	1.01040	1.01038	0.00005
7	1997	67	0.99321	0.99321	0.99321	0.00000	0.99331	0.99330	0.99331	-0.00001
9	1997	67	1.01168	1.01168	1.01168	0.00000	1.01134	1.01128	1.01131	-0.00006
10	1997	67	0.99277	0.99271	0.99274	-0.00006	0.99251	0.99251	0.99251	0.00000
1	1998	67	1.01208	1.01208	1.01208	0.00000	1.01155	1.01156	1.01156	0.00001
2	1998	67	0.99281	0.99281	0.99281	0.00000	0.99249	0.99257	0.99253	0.00008
3	1998	67	0.99411	0.99411	0.99411	0.00000	0.99448	0.99430	0.99439	-0.00018
4	1998	67	0.99291	0.99291	0.99291	0.00000	0.99286	0.99288	0.99287	0.00002
6	1998	67	1.01063	1.01053	1.01058	-0.00010	1.01037	1.01044	1.01041	0.00007
7	1998	67	0.99281	0.99286	0.99284	0.00005	0.99251	0.99251	0.99251	0.00000
10	1998	67	0.99336	0.99336	0.99336	0.00000	0.99335	0.99335	0.99335	0.00000
11	1998	67	0.99316	0.99316	0.99316	0.00000	0.99291	0.99303	0.99297	0.00012
12	1998	67	1.01048	1.01048	1.01048	0.00000	1.00992	1.00991	1.00992	-0.00001
1	1999	67	0.99376	0.99371	0.99374	-0.00005	0.99334	0.99331	0.99333	-0.00003
2	1999	67	0.99291	0.99282	0.99287	-0.00009	0.99247	0.99254	0.99251	0.00007
3	1999	67	0.99391	0.99386	0.99389	-0.00005	0.99359	0.99361	0.99360	0.00002
4	1999	67	1.01163	1.01163	1.01163	0.00000	1.01073	1.01078	1.01076	0.00005
7	1999	67	1.01028	1.01028	1.01028	0.00000	1.00978	1.00974	1.00976	-0.00004
8	1999	67	0.99256	0.99261	0.99259	0.00005	0.99240	0.99235	0.99238	-0.00005
10	1999	67	0.99256	0.99261	0.99259	0.00005	0.99240	0.99235	0.99238	-0.00005
11	1999	67	1.01168	1.01158	1.01163	-0.00010	1.01113	1.01122	1.01118	0.00009
12	1999	67	0.99336	0.99336	0.99336	0.00000	0.99317	0.99327	0.99322	0.00010
2	2000	67	0.99251	0.99246	0.99249	-0.00005	0.99220	0.99241	0.99231	0.00021
4	2000	67	0.99386	0.99386	0.99386	0.00000	0.99375	0.99380	0.99378	0.00005
5	2000	67	1.01328	1.01328	1.01328	0.00000	1.01276	1.01270	1.01273	-0.00006
		mean	1.00141	1.00142	1.00142	0.000012	1.00125	1.00126	1.00125	0.000017
		std.dev	0.01612	0.01612	0.01612	0.000085	0.01595	0.01598	0.01596	0.000078
Sr						0.000061				0.000056
r						0.000169				0.000157

Table 2: Simple statistics of specific gravity and alcoholic strength of 27 samples analysed in inter-laboratory ring test.
Legenda:R = red, W = white, Rs = rosè, D = dry, Sp = sparkling, Sw = sweet

Year	Monthly sample	Wine type	Specific gravity @ 20°C (g/cm3)							Alcoholic strength (% vol)						
			Hydrostatic balance			Electronic density-meter			a-b	Hydrostatic balance			Electronic density-meter			A-B
			mean (a)	std.dev.	n° of analyses	mean (b)	std.dev.	n° of analyses		mean (A)	std.dev.	n° of analyses	mean (B)	std.dev.	n° of analyses	
1999	1	Rs	0.99357	0.000108	38	0.99354	0.000133	30	0.00003	11.04	0.054	29	11.03	0.084	36	0.01
1999	2	W	0.99274	0.000094	33	0.99263	0.000137	25	0.00011	11.25	0.076	25	11.25	0.092	37	0.00
1999	3	R-D	0.99369	0.000124	40	0.99371	0.000203	39	-0.00001	11.94	0.058	31	11.97	0.059	42	-0.03
1999	4	W-Sp-Sw	1.01116	0.000110	28	1.01108	0.000177	34	0.00009	7.66	0.053	24	7.64	0.048	37	0.02
1999	5	Rs	0.99425	0.000119	40	0.99429	0.000117	39	-0.00003	11.19	0.098	32	11.19	0.066	42	0.00
1999	6	W	0.99225	0.000124	39	0.99225	0.000113	40	0.00000	11.27	0.093	34	11.30	0.051	42	-0.03
1999	7	R-Sp	1.01002	0.000201	38	1.00993	0.000185	39	0.00009	8.00	0.101	31	8.03	0.061	42	-0.03
1999	9	R-D	0.99367	0.000181	37	0.99370	0.000097	33	-0.00003	11.23	0.101	32	11.23	0.059	34	0.00
1999	10	W	0.99248	0.000133	34	0.99242	0.000066	35	0.00005	11.04	0.093	26	11.02	0.061	38	0.02
1999	11	W-Sp-Sw	1.01144	0.000142	30	1.01136	0.000152	35	0.00009	7.69	0.091	22	7.65	0.058	42	0.04
1999	12	Rs	0.99317	0.000128	35	0.99319	0.000075	29	-0.00001	11.00	0.061	28	11.00	0.069	31	0.00
2000	1	R-D	0.99356	0.000116	35	0.99366	0.000114	34	-0.00010	11.30	0.083	26	11.25	0.051	44	0.05
2000	2	W	0.99233	0.000143	37	0.99234	0.000133	38	-0.00001	11.24	0.068	28	11.24	0.057	37	0.00
2000	4	R-D	0.99386	0.000152	42	0.99381	0.000062	37	0.00005	11.22	0.077	32	11.22	0.049	38	-0.01
2000	5	W-Sp-Sw	1.01307	0.000267	42	1.01301	0.000229	39	0.00007	7.44	0.053	32	7.43	0.091	42	0.01
2000	6	W	0.99244	0.000157	35	0.99244	0.000126	40	0.00000	11.17	0.088	30	11.18	0.077	46	-0.01
2000	7	Rs	0.99309	0.000156	36	0.99306	0.000062	38	0.00003	10.85	0.065	28	10.84	0.076	40	0.01
2000	9	R-D	0.99411	0.000135	28	0.99414	0.000104	42	-0.00003	12.03	0.084	24	11.99	0.092	44	0.04
2000	10	W-D	0.99120	0.000143	27	0.99128	0.000102	45	-0.00008	11.37	0.098	30	11.35	0.065	43	0.02
2000	11	W-Sp	1.01301	0.000286	28	1.01296	0.000184	51	0.00005	7.65	0.085	30	7.61	0.062	54	0.04
2000	12	R-D	0.99376	0.000149	30	0.99379	0.000108	47	-0.00003	11.31	0.075	30	11.32	0.055	49	-0.01
2001	1	Rs	0.99258	0.000108	36	0.99250	0.000096	53	0.00008	11.41	0.087	34	11.43	0.054	58	-0.02
2001	2	W-D	0.99289	0.000109	29	0.99288	0.000102	55	0.00001	11.35	0.071	32	11.32	0.056	58	0.03
2001	3	R-D	0.99445	0.000172	28	0.99444	0.000090	69	0.00002	11.81	0.096	28	11.83	0.069	68	-0.02
2001	4	W-D	0.99270	0.000152	30	0.99267	0.000106	58	0.00003	11.33	0.070	30	11.34	0.072	62	-0.01
2001	5	R-Sp	1.01125	0.000199	30	1.01131	0.000154	62	-0.00006	8.06	0.068	34	8.06	0.071	56	0.00
		mean (n=26)	**0.997413**	**0.000150**		**0.997398**	**0.000124**		**0.000015**	**10.493**	**0.079**		**10.489**	**0.066**		**0.005**
		std.dev.	**0.008006**	**0.000046**		**0.007986**	**0.000044**		**0.000055**	**1.558**	**0.016**		**1.564**	**0.013**		**0.023**
		SR		**0.000111**			**0.000093**				**0.057**			**0.047**		
		R		**0.000311**			**0.000260**				**0.159**			**0.132**		
2000	3	White juice	1.07655	0.002350	20	1.07638	0.002293	28	0.00016	0.64	0.232	18	0.56	0.340	24	0.08

Figure 1: Regression line of the specific gravity computed on the basis of the mean value of 2 subsequent measures carried out on samples (n=62) analysed in 3 different laboratories

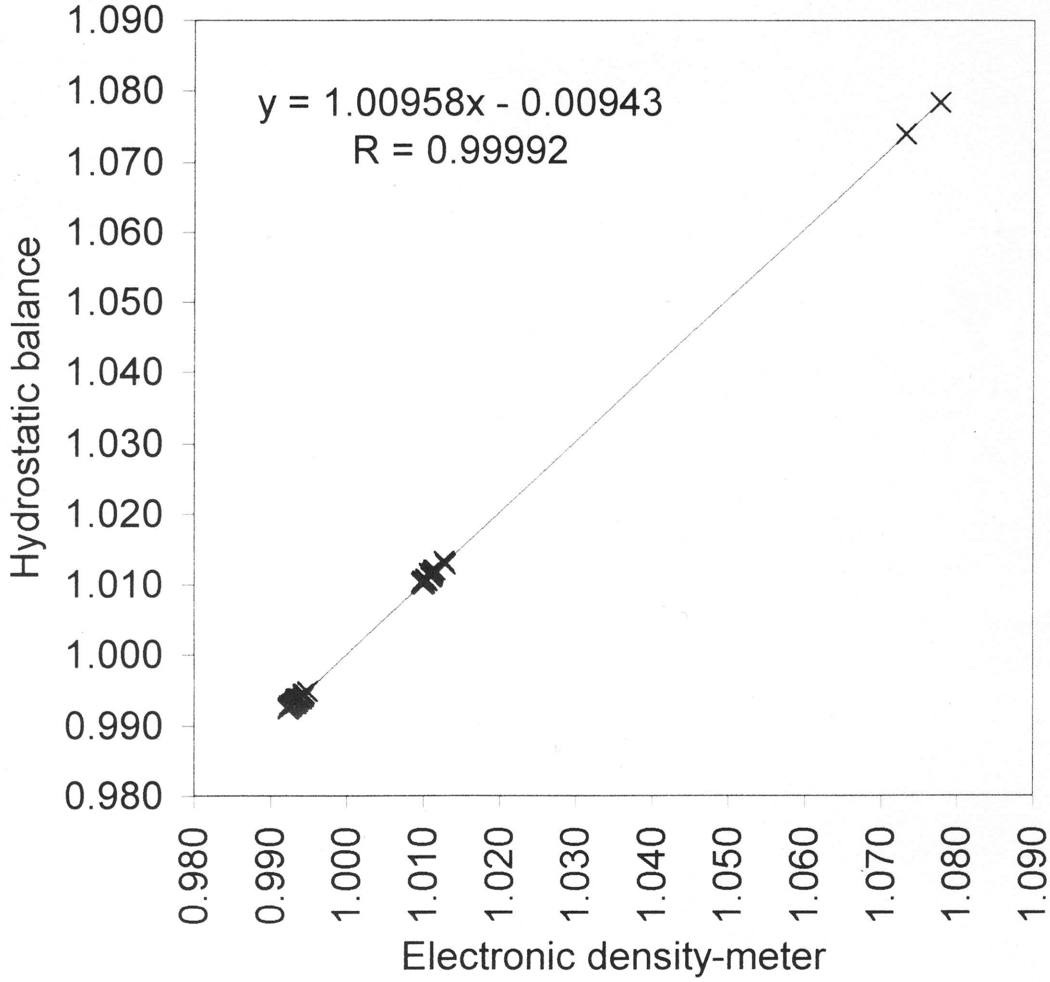
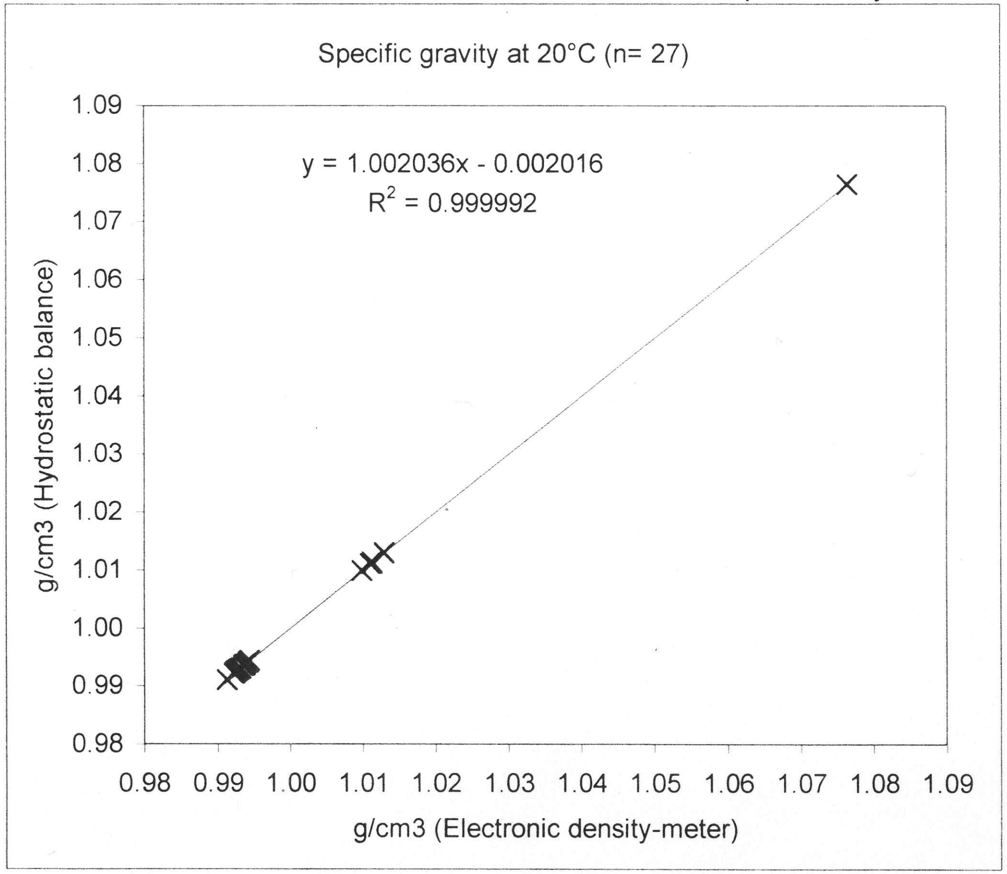
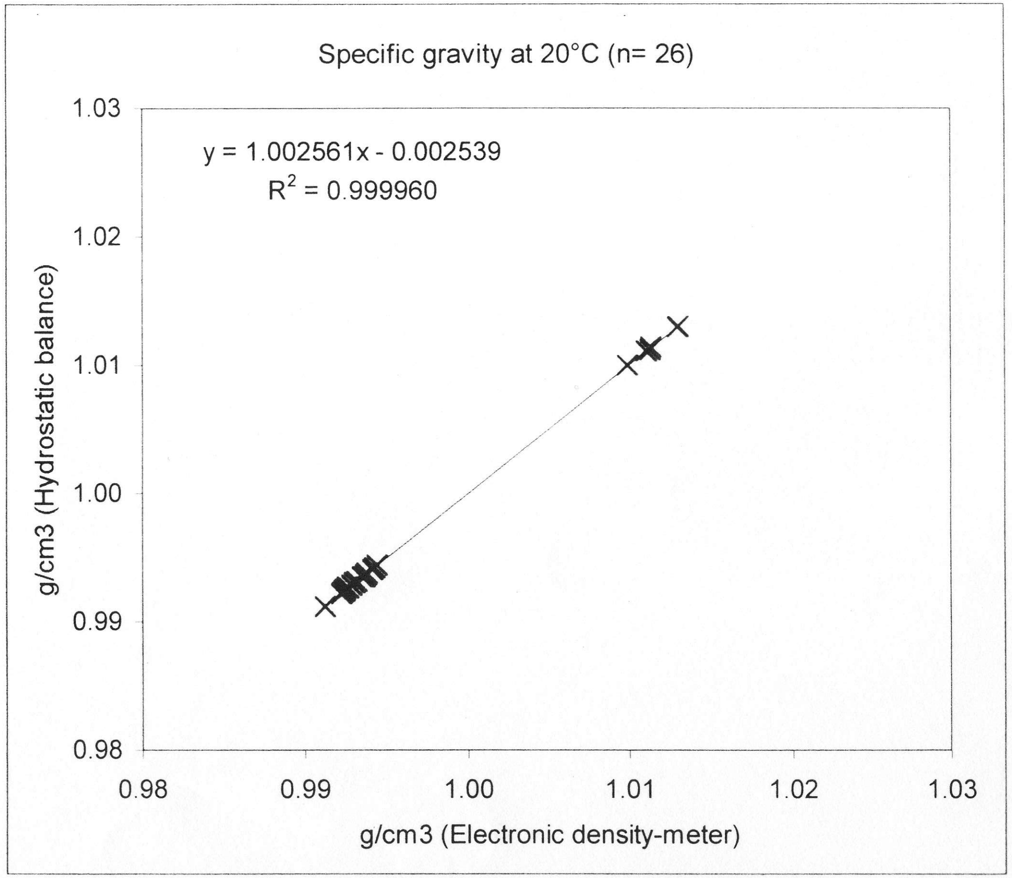


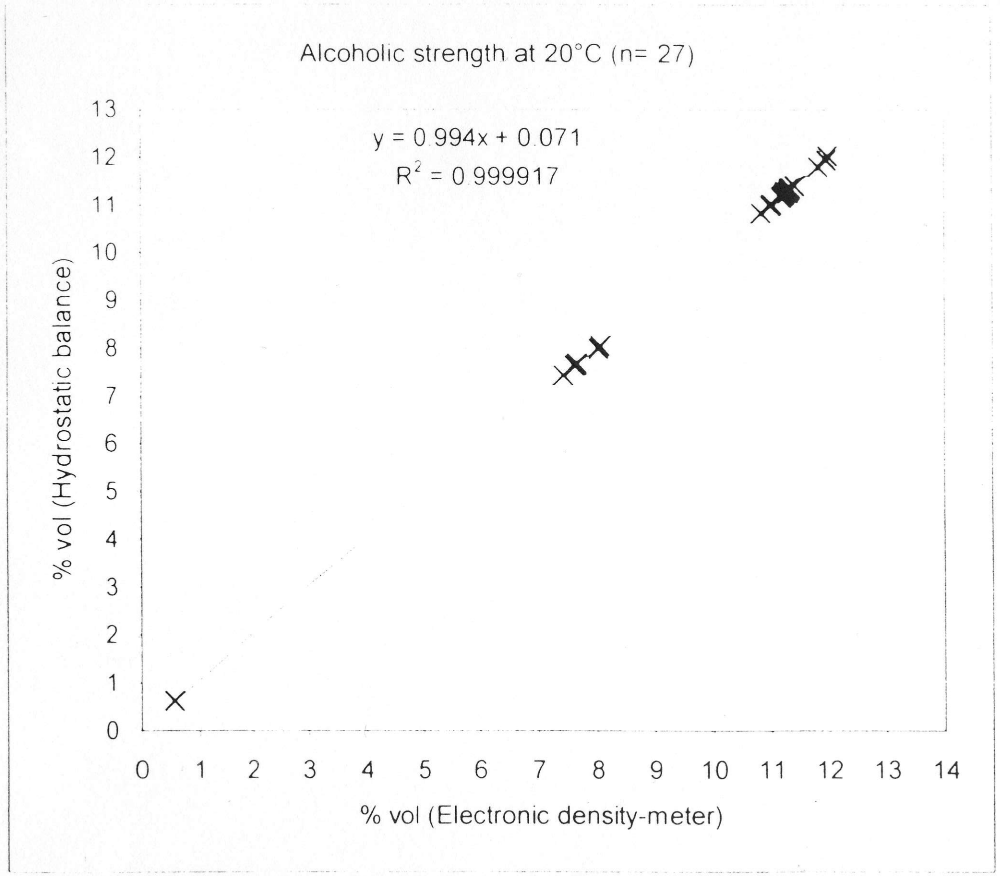
Figure 2: Regression line of the specific gravity computed almost on the basis of the mean value of 2 subsequent measures carried out on samples analysed in several different laboratories

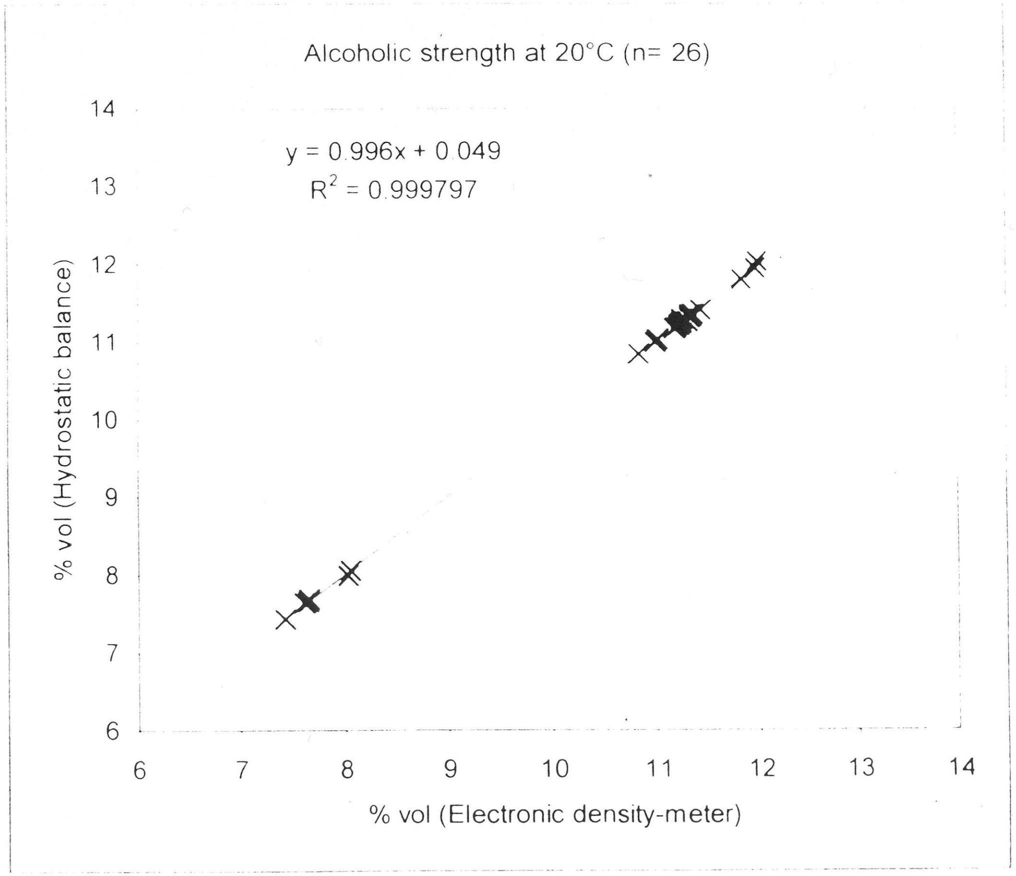




The same relationship without the sample at the highest density

Figure 3: Regression line of the alcoholic strength computed almost on the basis of the mean value of 2 subsequent measures carried out on samples analysed in several different laboratories





The same relationship without the sample at the lowest alcoholic strength

Figure 4. Specific gravity (g/cm3): differences between mean data achieved by hydrostatic balance (a) and electronic density-meter (b) (n=26)

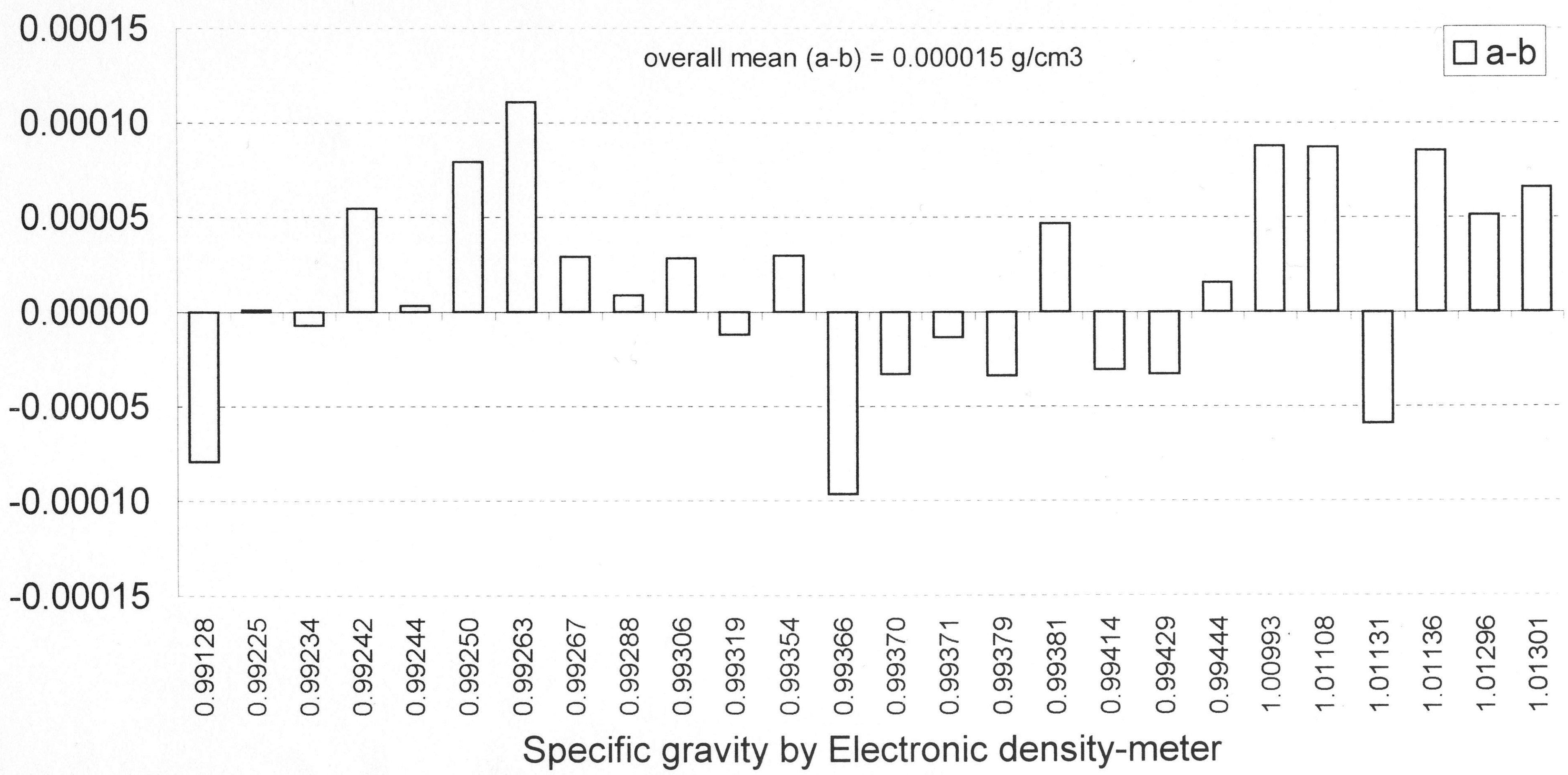


Figure 5: Alcoholic strength (% vol): differences between mean data achieved by hydrostatic balance (A) and electronic density-meter (B) (n=26)