

## STATISTICAL METHODOLOGY FOR VALIDATION CALIBRATION METHODS IN HYDROMETRY

*Maria do Céu Ferreira<sup>1</sup>, José Mendonça Dias<sup>2</sup>*

<sup>1</sup> Portuguese Institute for Quality, Central Laboratory of Metrology, 2829-516 CAPARICA, Portugal.  
mcferreira@mail.ipq.pt

<sup>2</sup> Department of Mechanical and Industrial Engineering, Faculty of Sciences and Technology,  
Universidade Nova de Lisboa, Quinta da Torre, 2829-516 CAPARICA, Portugal.  
jad@fct.unl.pt

**Abstract:** The main purpose of this paper is to study the uncertainty budget of hydrometers calibration and the error of Cuckow's method according the Signal-to-Noise Ratio Taguchi approach in order to analyse this two different kinds of methodology. The calibration of density hydrometers is influenced by some parameters; in order to research the influence of these factors in the measuring value, an experimental design with dynamic characteristics was applied. With this methodology, five control factors were considered, at two levels each and a L<sub>32</sub> Orthogonal Array was defined. It was evaluated the influence of each parameter (factor) and the interaction between them according Cuckow's method and Taguchi methodologies. The simultaneous analysis of the error and the sensitivity leads to a proper choice of significant control factors and respective best levels in order to reduce the variability of the measurement system.

**Keywords:** Density, Hydrometers, Taguchi, Signal-to-Noise Ratio, Dynamic Characteristics.

### 1. INTRODUCTION

Hydrometers are density liquids measuring instruments used in several fields which traceability to SI is provided by National Laboratory of Metrology. A basic tool in ensuring this traceability is measuring instrument calibration.

Measurement of liquid density plays a major role in the quality assurance of production processes. The density of liquids is measured in a wide range of process industries, such as pharmaceutical, food, agrochemical and petrochemical. Beside other measurements methods the use of hydrometers is one of the most employed by majority industrial laboratories.

A hydrometer can be calibrated with the reference liquids, where it freely floats in one of its graduation marks at the same plane of the level surface of the liquid.

Portuguese Institute for Quality adopts the hydrostatic weighing method for hydrometers calibration using a single liquid whose density is not deliberately altered throughout the whole process. In this study, a density hydrometer was calibrated in three scale graduation marks using n-Nonane as reference liquid by Cuckow method, which is based on the Archimedes' principle

$$\rho = (\rho_{liq} - \rho_{al}) \frac{w_{ar} + \varphi \times \lambda_{pt}}{w_{ar} - w_{liq} \left[ 1 - \left( \frac{\rho_{ar} - \rho_{al}}{\rho_{wt}} \right) \right] + \varphi \times \lambda_{liq}} [1 + \alpha \times (t_{liq} - t_{ref})] + \rho_{al} \quad (1)$$

where:

$\rho_{liq}$  - The density of the liquid in which the hydrometer is weighed,

$\rho_{al}$  - The density of the air in which the hydrometer is weighed,

$w_{ar}$  - The weight of the hydrometer in air of density  $\rho_{aa}$ ,

$w_{liq}$  - The apparent weight of the hydrometer in liquid of density  $\rho_{al}$ ,

$\lambda_{pt}$  - Reference surface tension (at scale line),

$\lambda_{liq}$  - Liquid surface tension of test liquid,

$\alpha$  - Cubic expansion coefficient (25E-06),

$\varphi = \frac{\pi \times d}{g}$  - where  $d$  is the diameter of hydrometer' stem at meniscus level and  $g$  the gravity acceleration.

For the calibration of hydrometers, all parameters must be known, including their uncertainty.

### 2. CALIBRATION RESULTS AND UNCERTAINTY BUDGET

From equation (1), the density of each reference value was obtained by experimental method at 20 °C which values are shown in Table 1.

Table 1: Calibration results at 20 °C

Indication g/cm <sup>3</sup>	Conventional true value g/cm <sup>3</sup>
1,0035	1,00325
1,0065	1,00629
1,0095	1,00935

In order to evaluate the uncertainty of calibration in accordance to the GUM [2], the values of the several contributions to combined standard uncertainty are summarized in Tables 2, 3 and 4.

**Table 2: Expanded uncertainty for the reference value of 1,00325 g/cm<sup>3</sup>**

Standard uncertainty component $u(x_i)$	Unit	Value $(x_i)$	Value of standard uncertainty $y u(x_i)$	Value of sensitivity coefficient $C_i$	Contribution to the combined standard uncertainty $u_i(y)$ g/cm <sup>3</sup>
$u(t_{ref})$	°C	20	2,50E-03	-2,505E-05	-6,26E-08
$u(t_{liq})$	°C	20,1	2,50E-03	2,505E-05	6,26E-08
$u(l_{pt})$	(mN/m)	75	4,91E-02	9,477E-06	4,65E-07
$u(l_{liq})$	(mN/m)	22,9	2,50E-02	-1,325E-05	-3,31E-07
$u(r_{liq})$	g/cm <sup>3</sup>	0,717958	4,64E-06	1,398E+00	6,48E-06
$u(r_{al})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-3,448E-01	-1,21E-06
$u(r_{ar})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-4,977E-02	-1,75E-07
$u(r_{wt})$	g/cm <sup>3</sup>	8	2,89E-05	0,000E+00	0,00E+00
$u(w_{liq})$	g	42,7500	6,58E-05	3,066E-02	2,02E-06
$u(w_{ar})$	g	150,312	1,57E-04	-2,651E-03	-4,17E-07
$u(a)$	1/K	2,5E-05	1,45E-05	1,002E-01	1,45E-06
$u(d)$	cm	0,444	1,10E-03	9,175E-04	1,01E-06
$U_c = 7,16E-06$ ; Degrees of freedom = 1,195E+23; Expanded uncertainty U(y) for a confidence level of 95% = 1,43E-05					

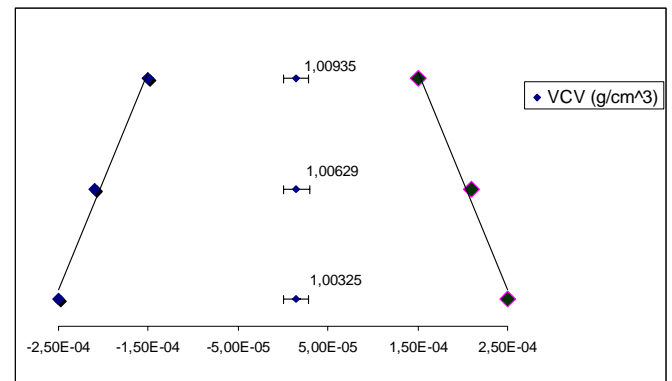
**Table 3: Expanded uncertainty for the reference value of 1,00629 g/cm<sup>3</sup>**

Standard uncertainty component $u(x_i)$	Unit	Value $(x_i)$	Value of standard uncertainty $u(x_i)$	Value of sensitivity coefficient $C_i$	Contribution to the combined standard uncertainty $u_i(y)$ g/cm <sup>3</sup>
$u(t_{ref})$	°C	20	2,50E-03	-2,513E-05	-6,28E-08
$u(t_{liq})$	°C	20,1	2,50E-03	2,513E-05	6,28E-08
$u(l_{pt})$	(mN/m)	75	4,91E-02	9,505E-06	4,66E-07
$u(l_{liq})$	(mN/m)	22,9	2,50E-02	-1,333E-05	-3,33E-07
$u(r_{liq})$	g/cm <sup>3</sup>	0,717958	4,64E-06	1,402E+00	6,50E-06
$u(r_{al})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-3,518E-01	-1,23E-06
$u(r_{ar})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-5,045E-02	-1,77E-07
$u(r_{wt})$	g/cm <sup>3</sup>	8	2,89E-05	0,000E+00	0,00E+00
$u(w_{liq})$	g	43,0756	1,01E-04	3,085E-02	3,10E-06
$u(w_{ar})$	g	150,3122	1,26E-04	-2,687E-03	-3,38E-07
$u(a)$	1/K	2,5E-05	1,45E-05	1,005E-01	1,46E-06
$u(d)$	cm	0,444	1,10E-03	9,182E-04	1,01E-06
$U_c = 7,55E-06$ ; Degrees of freedom = 1,842E+23; Expanded uncertainty U(y) for a confidence level of 95% = 1,51E-05					

**Table 4: Expanded uncertainty for the reference value of 1,00935 g/cm<sup>3</sup>**

Standard uncertainty component $u(x_i)$	Unit	Value $(x_i)$	Value of standard uncertainty $u(x_i)$	Value of sensitivity coefficient $C_i$	Contribution to the combined standard uncertainty $u_i(y)$ g/cm <sup>3</sup>
$u(t_{ref})$	°C	20	2,50E-03	-2,520E-05	-6,30E-08
$u(t_{liq})$	°C	20,1	2,50E-03	2,520E-05	6,30E-08
$u(l_{pt})$	(mN/m)	75	4,91E-02	9,534E-06	4,68E-07
$u(l_{liq})$	(mN/m)	22,9	2,50E-02	-1,341E-05	-3,35E-07
$u(r_{liq})$	g/cm <sup>3</sup>	0,717958	4,64E-06	1,407E+00	6,52E-06
$u(r_{al})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-3,554E-01	-1,25E-06
$u(r_{ar})$	g/cm <sup>3</sup>	0,001170	3,51E-06	-5,114E-02	-1,80E-07
$u(r_{wt})$	g/cm <sup>3</sup>	8	2,89E-05	0,000E+00	0,00E+00
$u(w_{liq})$	g	43,4010	6,26E-05	3,103E-02	1,94E-06
$u(w_{ar})$	g	150,3122	1,26E-04	-2,724E-03	-3,43E-07
$u(a)$	1/K	2,5E-05	1,45E-05	1,008E-01	1,46E-06
$u(d)$	cm	0,444	1,10E-03	9,189E-04	1,01E-06
$U_c = 7,18E-06$ ; Degrees of freedom = 1,142E+23; Expanded uncertainty U(y) for a confidence level of 95% = 1,44E-05					

Figure 1 summarizes calibration results with the value of uncertainty.



**Figure 1: Uncertainty of calibration**

### 3 ANALYSIS OF THE DENSITY HYDROMETER ERRORS USING TAGUCHI'S SN RATIO

After the analysis of the parameters related with the calibration of the density hydrometer, was carried out an experimental layout with five control factors, at two levels each, as follows:

- A – Ambient temperature in the range of 17 °C to 23 °C;
- B – Atmospheric pressure in the range of 900 hPa to 1900 hPa;
- C – Superficial tension of n-Nonane in the range of 21 mN/m to 25 mN/m;
- D – Liquid temperature in the range of 18 °C to 22 °C;
- E- Humidity in the range of 45% to 80%.

Table 5 shows the Orthogonal Array ( $L_{32}$ ) obtained for this calibration study.

Table 5: Design Array

n	A	B	C	D	E
1	1	1	1	1	1
2	2	1	1	1	1
3	1	2	1	1	1
4	2	2	1	1	1
5	1	1	2	1	1
6	2	1	2	1	1
7	1	2	2	1	1
8	2	2	2	1	1
9	1	1	1	2	1
10	2	1	1	2	1
11	1	2	1	2	1
12	2	2	1	2	1
13	1	1	2	2	1
14	2	1	2	2	1
15	1	2	2	2	1
16	2	2	2	2	1
17	1	1	1	1	2
18	2	1	1	1	2
19	1	2	1	1	2
20	2	2	1	1	2
21	1	1	2	1	2
22	2	1	2	1	2
23	1	2	2	1	2
24	2	2	2	1	2
25	1	1	1	2	2
26	2	1	1	2	2
27	1	2	1	2	2
28	2	2	1	2	2
29	1	1	2	2	2
30	2	1	2	2	2
31	1	2	2	2	2
32	2	2	2	2	2

Following the approach in Yano, H. (1991), a standard linear regression model is fitted for each row of Table 5 using the set of observations obtained for experimental results. Thus, for  $i^{\text{th}}$  row of Table 6 the model

$$y_i = m + \beta(M_i - \bar{M}) + \varepsilon \quad (2)$$

is fitted using least squares regression, where:

y - Indication value,

m - Mean of indication value,

$\bar{M}$  - True value,

$\bar{M}$  - Mean of true value

$\beta$  - Ratio of covariance's

$\varepsilon$  - Calibration error

The value of  $\beta$  is selected in order to minimize the total of the squares of differences between the left side and the right side of the equation. The value of  $\beta$  that minimizes equation is given by:

$$\hat{\beta} = \frac{1}{r} [(M_1 - \bar{M})y_1 + (M_2 - \bar{M})y_2 + \dots + (M_k - \bar{M})y_k] \quad (3)$$

Where r is estimated by:

$$r = r_0 \sum_{i=1}^K (M_i - \bar{M})^2 \quad (4)$$

and  $\bar{M}$  by:

$$\bar{M} = \frac{(M_1 + M_2 + M_k)}{k} \quad (5)$$

The variation caused by linear effect, denoted by  $S_\beta$  is given by:

$$S_\beta = \frac{1}{r} \left[ \sum_{i=1}^K (M_i - \bar{M})y_i \right]^2 \quad (6)$$

The error variation, including the deviation from linearity  $V_e$ , is:

$$S_e = S_T - S_\beta \quad (7)$$

The error variance is the error variation divided by its degrees of freedom.

$$V_e = \frac{S_e}{kr_0 - 2} = \frac{S_T - S_\beta}{kr_0 - 2} \quad (8)$$

For this application, signal-response is estimated in decibels by:

$$\eta = 10 \log \frac{\frac{1}{r}(S_\beta - V_e)}{V_e} \quad (dB) \quad (9)$$

The raw data obtained for each experimental run, along with its associated Signal-to-Noise Ratio are summarized in Table 6.

**Table 6: Raw data for each experiment al results**

n	Medium of convencional true value			FC	r	Sb	ST	Verror	Serror	S/N (dB)
1	1,00461	1,00765	1,01072	9,1174	5,87E-05	5,14E-05	0	3,68E-07	2,58E-06	63,732
2	1,00428	1,00732	1,01038	9,1174	6,16E-05	4,90E-05	0	7,08E-07	4,96E-06	60,449
3	1,00398	1,00702	1,01008	9,1174	6,15E-05	4,90E-05	5,40E-05	7,18E-07	5,02E-06	60,387
4	1,00432	1,00736	1,01042	9,1174	5,95E-05	5,07E-05	0	4,70E-07	3,29E-06	62,548
5	1,00479	1,00783	1,01089	9,1174	5,78E-05	5,23E-05	0	2,38E-07	1,67E-06	65,778
6	1,00445	1,00750	1,01056	9,1174	6,00E-05	5,03E-05	0	5,22E-07	3,66E-06	62,007
7	1,00449	1,00753	1,01059	9,1174	5,70E-05	5,29E-05	0	1,57E-07	1,10E-06	67,699
8	1,00467	1,00771	1,01077	9,1174	5,82E-05	5,19E-05	0	3,02E-07	2,11E-06	64,686
9	1,00181	1,00484	1,00790	9,1174	5,77E-05	5,21E-05	0	2,71E-07	1,90E-06	65,211
10	1,00147	1,00451	1,00756	9,1174	5,76E-05	5,21E-05	0	2,74E-07	1,92E-06	65,164
11	1,00119	1,00423	1,00728	9,1174	5,81E-05	5,16E-05	0	3,48E-07	2,44E-06	64,033
12	1,00138	1,00442	1,00747	9,1174	5,66E-05	5,29E-05	0	1,49E-07	1,04E-06	67,958
13	1,00143	1,00446	1,00752	9,1174	5,78E-05	5,19E-05	0	2,91E-07	2,04E-06	64,869
14	1,00148	1,00451	1,00756	9,1174	5,71E-05	5,25E-05	0	2,01E-07	1,40E-06	66,608
15	1,00126	1,00429	1,00760	9,1174	6,25E-05	5,20E-05	0	2,80E-07	1,96E-06	64,709
16	1,00151	1,00455	1,00760	9,1174	5,85E-05	5,12E-05	0	3,90E-07	2,73E-06	63,476
17	1,00440	1,00745	1,01051	9,1174	6,13E-05	4,93E-05	0	6,74E-07	4,72E-06	60,707
18	1,00441	1,00745	1,01052	9,1174	6,13E-05	4,93E-05	0	6,76E-07	4,73E-06	60,695
19	1,00411	1,00715	1,01021	9,1174	6,02E-05	5,01E-05	0	5,58E-07	3,90E-06	61,691
20	1,00412	1,00716	1,01022	9,1174	6,02E-05	5,01E-05	0	5,62E-07	3,94E-06	61,651
21	1,00432	1,00736	1,01042	9,1174	6,18E-05	4,89E-05	0	7,33E-07	5,13E-06	60,269
22	1,00432	1,00737	1,01043	9,1174	6,18E-05	4,89E-05	0	7,35E-07	5,14E-06	60,251
23	1,00448	1,00753	1,01059	9,1174	5,71E-05	5,28E-05	0	1,70E-07	1,19E-06	67,350
24	1,00442	1,00746	1,01052	9,1174	5,75E-05	5,24E-05	0	2,22E-07	1,56E-06	66,114
25	1,00187	1,00497	1,00803	9,1174	5,95E-05	5,15E-05	0	3,52E-07	2,46E-06	63,879
26	1,00187	1,00491	1,00796	9,1174	5,81E-05	5,17E-05	0	3,24E-07	2,27E-06	64,360
27	1,00154	1,00458	1,00763	9,1174	5,86E-05	5,12E-05	0	4,07E-07	2,85E-06	63,284
28	1,00146	1,00449	1,00756	9,1174	5,92E-05	5,06E-05	0	4,85E-07	3,39E-06	62,421
29	1,00173	1,00477	1,00782	9,1174	5,85E-05	5,13E-05	0	3,85E-07	2,69E-06	63,545
30	1,00173	1,00476	1,00781	9,1174	5,91E-05	5,08E-05	0	4,52E-07	3,16E-06	62,760
31	1,00151	1,00455	1,00760	9,1174	6,02E-05	4,98E-05	0	6,00E-07	4,20E-06	61,341
32	1,00153	1,00456	1,00761	9,1174	6,02E-05	4,98E-05	0	5,94E-07	4,16E-06	61,392

**Table 7: ANOVA**

### 3.1 ANALYSIS OF VARIANCE

The main purpose of this of this methodology is to identify the principal factors that can induce error increase in order to create conditions for minimize the variability of the measurement system.

Analysis of Variance (ANOVA), is an important Statistic Tool that can validated the selection of factors and levels which minimize the ratio S/N. A result of this condensed analysis is presents in Table 7. The so-called net contribution ( $\rho$ ) is also presented for significant effects.

Factor	SS	g.l.	MS	F0	p
D	11,278	1	11,278	4,763	0,038
E	23,808	1	23,808	10,054	0,004
B x D	21,155	1	21,155	8,934	0,006
C x D	27,945	1	27,945	11,801	0,002
B x C x D	16,24	1	16,239	6,858	0,015
Erro	61,566	26	2,368		
Total SS	161,992	31			

According to ANOVA results, the following conclusions are reached:

- i) There is evidence that factors D and E have an impact on S/N value and the best levels to reduce variation will be level 2 for liquid temperature (D) and level 1 to humidity (E) (Figure. 2).

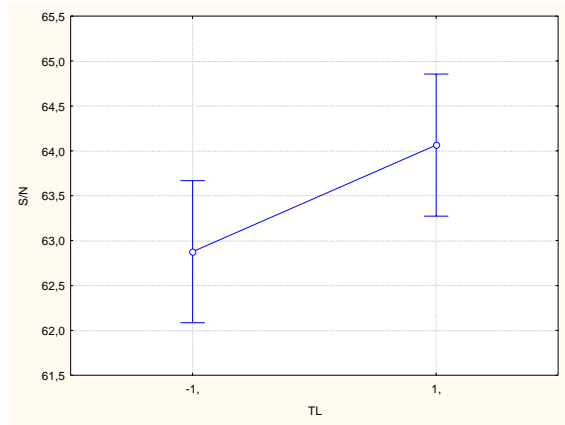


Figure 2: S/N plot for liquid temperature

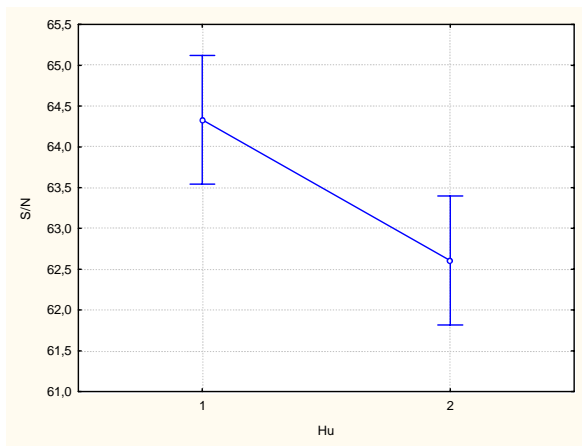


Figure 3: S/N plot for humidity

- ii) The interaction between BxD and CxD have significant effects on S/N; for the first interaction the best levels to reduce variation will be the level 1 for pressure (B) and level 2 for liquid temperature (D). For the interaction CxD, the best levels to reduce variation will be the level 1 for surface tension (C) and level 2 for liquid temperature (D).

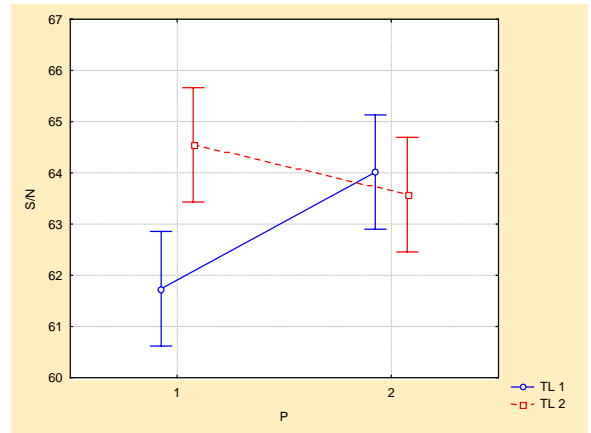


Figure 4: Joint effects plots for Interaction between pressure and liquid temperature

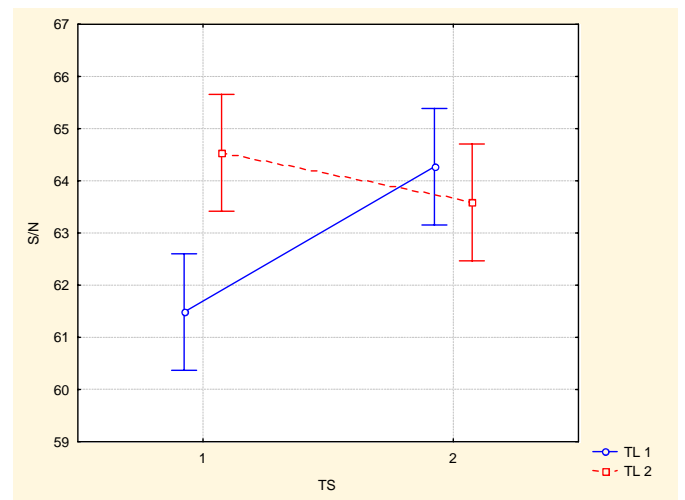


Figure 5: Joint effects plots for interaction between Interaction between surface tension and liquid temperature

- iii) The interaction between BxCxD is also ambiguous. The best levels for pressure (B) and surface tension (C) is the level 2 and the level 1 optimize the contribution of liquid temperature (D). A possible explanation for these results can be related by the effects of the factors when interact which significant influences are modify.

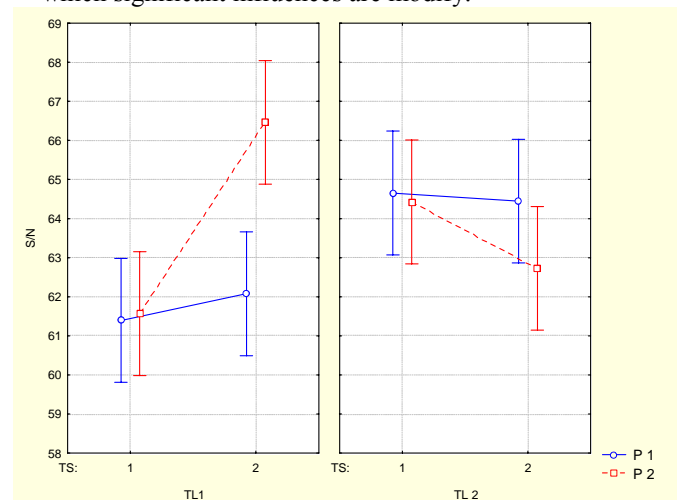


Figure 6: Joint effects plots for Interaction between pressure, liquid temperature and surface tension

The plot of Figure 7 allows assuming that all residuals are in accordance with a Normal distribution.

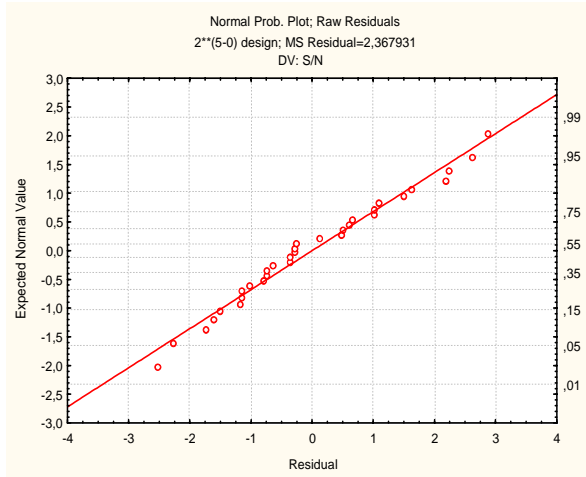


Figure 7: Normality of residues

As a result of this study, the best levels of control factors to increase the ratio S/N of this calibration process are: TL<sub>2</sub>; HU<sub>1</sub>; P<sub>1</sub>TL<sub>2</sub>; TS<sub>1</sub>TL<sub>2</sub>; P<sub>2</sub>TS<sub>2</sub>TL<sub>1</sub>.

### 3.2 TAGUCHI MEASUREMENT ERROR

According Yano (1991), the measurement error is defined by,

$$V_e' = \frac{1}{\eta}, \text{ and } S/N = 10 \log \eta = 67,43$$

$$\eta = 10^{\left(\frac{67,4279}{10}\right)} = 3,69E + 06$$

$$V_e' = \frac{1}{3,69E + 06} = 2,71E - 07$$

$$V_e' = 2,71E - 07$$

which value was obtained by the confirmatory experiment for the best levels of the significant factors.

Thus, the standard deviation of measurement error,  $s'$ , is the square root of variance,  $s' = \sqrt{2,71E - 07}$ ,

$$s' = 5,2E - 04 \quad (g/cm^3)$$

### 4. CONCLUSION

The analysis of data from parameter design experiments for signal-response systems could help to better understand the importance of increasing linearity and sensitivity, and reducing variability.

In this paper it was applied Taguchi's methodology to a dynamic process – density hydrometer calibration- where was characterised the best levels of control factors which optimize the calibration procedure.

A comparative analysis between the error and uncertainty values obtained from hydrometer calibration by Cuckow's method and Taguchi methodology, show a gradient of

$8 \times 10^{-04} g/cm^3$ , which value is in agree with reproducibility conditions. The Taguchi error value includes the measurement error and the sum of variances in all range of density hydrometer scale.

This study deals with one common type of signal-response; other types exist and many require a somewhat modified analysis.

### REFERENCES

- [1] **F.W. Cuckow**: *New Method of High Accuracy for of the Calibration of Standard Hydrometers*, J. Soc. Chem. Ind., 68, pp. 44-49, 1949.
- [2] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, *Guide to the expression of uncertainty in measurement*, first edition, ISO Geneva, 1995.
- [3] **Taguchi, G.**, (1992), *Taguchi Methods: Research and Development*, American Supplier Institute, Inc.
- [4] **Taguchi, G.** (1993), *Taguchi on Robust technology Development: Bringing Quality engineering Upstream*, The American Society of Mechanical Engineers, 345 East 47th Street, New York, NY 10017-2392.
- [5] **Yano, H.** (1991), *Metrological Control*, Quality Resources, 1 Water Street, White Plains, , NY 10601