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NEUTRAL DENSITY FILTERS CALIBRATION FOR SPECTROPHOTOMETRIC LABORATORIES

CALIBRACIÓN DE FILTROS DE DENSIDAD NEUTRA PARA LABORATORIOS ESPECTROFOTOMÉTRICOS

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Abstract: Current regulations governing inspection of gaseous pollutants from diesel vehicles require, without exception, calibration certificates accompanying the neutral density filters. This article presents the research process for analysis and design of specialized software in Neutral (DN) density opacity lens calibration for spectrophotometric laboratories. In order to do this, it is taken as a reference the Circular No 98.00.852.005.1, issued by the French Ministry of Economy, Finance and Industry, Metrology Branch concerning the manner of construction, control and use of opacimeters; and is consistent with the Colombian technical standards NTC 4231 and NTC 17025 structured test. By the way, an implemented software exclusively *In Situ*, in the FENIX TYD laboratory for lens calibration certification, with national and international standardized details; In fulfillment of the traceability of the patterns and delivering an expanded uncertainty of 0.04U to 0.45U of the photometric scale - according to the normative requirement that establishes the maximum in 0.5U-.

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Keywords: Certification, spectrophotometer, traceability, transmittance, transmittance density, and uncertainty.

Resumen*:* La normatividad vigente que regula la inspección de gases contaminantes de vehículos diesel exige, sin excepción, el acompañamiento de certificados de calibración a los filtros de densidad neutra. El presente artículo presenta el proceso de investigación para el análisis y diseño de un software especializado en la calibración de lentes de opacidad de densidad neutra (DN), para laboratorios de espectrofotometría. Para lo anterior, se toma como referencia la circular nº 98.00.852.005.1, emanada del Ministerio de Economía francés; y se estructura una prueba consistente con las normas técnicas colombianas NTC 4231 y NTC 17025. Se obtiene así, un software implementado de manera exclusiva *In Situ* en el laboratorio FENIX TYD para la certificación de calibración de lentes, con precisiones estandarizadas nacionales e internacionales; cumpliéndose la trazabilidad de los patrones y entregando una incertidumbre expandida de 0,04*U* a 0,45*U* de la escala fotométrica -conforme al requisito normativo que establece el máximo en 0,5U-.

Palabras clave: Certificación, espectrofotómetro, trazabilidad, transmitancia, densidad de transmitancia, incertidumbre.

1. Introduction

The current Colombian law regulating the inspection of pollutants gaseous from diesel vehicles (NTC 4231) requires, without exception, calibration certificates of reference materials that verify the linearity processes in the opacity equipment. (Paragraphs 2.34 Verification of linearity; 4.2.2 linearity, 4.2.9 neutral density filters), [1].

Once this problem is established, opacimeter in Automotive Diagnostic Centers, vehicular environmental control authorities and entities and regional environmental inspection authorities of every city; have the responsibility of going in search of accredited laboratories or have the necessary international traceability and, in addition, owning measurement procedures attached to the 4231 NTC Colombian Technical Standard, [1]. The Colombian market Calibration Laboratories at this time do not have competence in the spectrophotometry area and therefore do not calibrate for reference materials in the magnitudes of transmittance or opacity, [2], Figure 1. The demand for this service requires certification for elements in European, American, or Central America laboratories. Consequently, the users have the obligation to submit reference materials overseas, increassing transportation and storage costs and risks.

Therefore, the FENIX Technology and Development Colombian Company implemented a technical, scientific, administrative and statistical measuring method in order to solve this need of spectrophotometry in a Colombian laboratory, offering strict fulfillment with national regulations in force and requirements for certification bodies. The method study, research, development and validation are attached directly to the specifications in the 17025 NTC Colombian Technical Standard, *General requirements for the competence of testing and calibration laboratories* [3].

Two types of calibration methods for ND filters are now known in the world. The first one is the method established by the Economy, Finance and Industry French Ministry. [4]; the second one is the Mexican method established by the National Metrology Mexican Center CENAM, [5]. This article is structured, first, by entering a brief identified issue and contextualization of the standards which must adhere to the developed method; it shows then, the research base for the

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development; then, its validation materials and methods from spectrophotometry and metrology; then the analysis and design of software which automate the method by own statistical analysis of metrology and statistics are shown. Finally, the results of the implementation of the software, its validation and response before direct users and environmental control agencies and accreditation bodies assessing and controlling them.

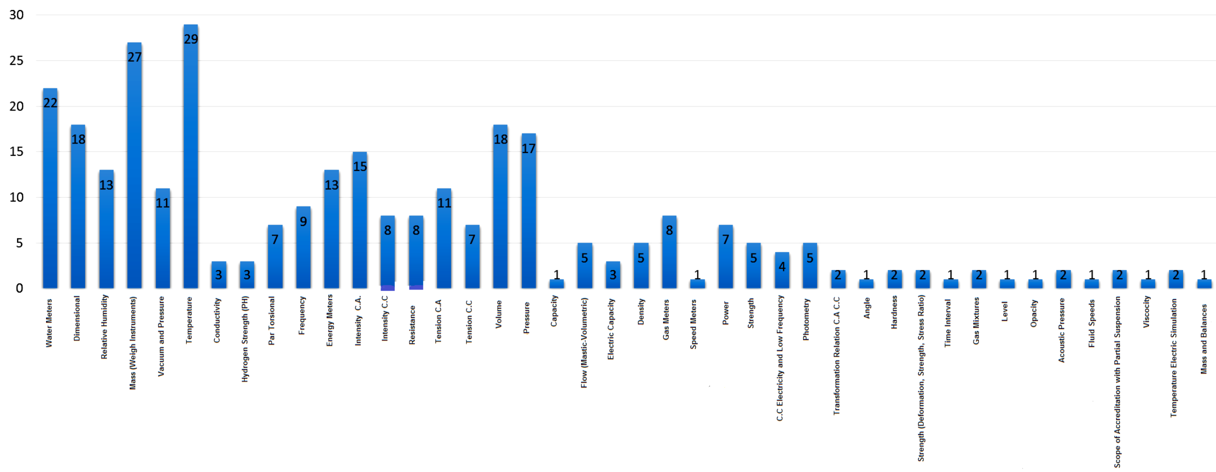

Figure 1. Accredited Laboratories by ONAC June 2015**.**

Source: ONAC Organismo Nacional de Acreditación Nacional.

2. Base research for development.

2.1 Metrology and calibration laboratories.

Metrology is the science and engineering of the measure. It includes the study, maintenance and application of the measurement management system. Its main objective is the acquisition and expression of the magnitude value, ensuring the processes traceability and the achievement of the required accuracy, [6]. In Colombia, the Commerce and Industry Superintendency (SIC), acts as a National Metrology Agency with scientific and industrial functions and as a national organization of legal metrology. INVIMA, ICA, the National Institute of Health and the IDEAM also meet metrology functions, [7]. The SIC derives 3 pillars of Colombian metrology: ICONTEC, responsible for the creation and publication of the Colombian technical standards; the INM, coordinates national patterns of scientific and industrial metrology through research; and the ONAC, responsible for laboratory accreditation in Colombia, [8][1].

Laboratory accreditation is a way to determine the technical competence of laboratories to perform specific types of tests or calibrations. At the moment of the accreditation, the laboratory obtains a formal recognition of their competence, providing customers a way to identify and select reliable testing services and able to meet their needs calibration, [9].

2.2 Spectrophotometry.

Spectrophotometry regards the quantitative methods of chemical analysis that use light to measure substance or material concentration. Depending on the radiation used, they are known as methods of visible absorption (colorimetry), ultraviolet method and infrared light method, [10]. The visible electromagnetic spectrum (light) belongs to wavelengths between 400 nm and 700 nm, [11]. When light passes through any material or solution three types of phenomena occur: Absorbance, transmittance and refraction. Spectrophotometry quantitatively analyzes these phenomena, [12].

2.2.1Transmittance [13], [14].

The amount of light transmitted through a solution is known as transmittance (T). This is defined as the ratio of the energy of light transmitted through a sample solution (I) and the energy

[1] INVIMA: Instituto Nacional de Medicamentos y Alimentos; ICA: Instituto Colombiano Agropecuario; IDEAM Instituto de hidrología, meteorología y estudios ambientales de Colombia; ICONTEC: Instituto colombiano de normas técnicas.

transmitted through a reference solution (I_0), also called White Reference, which is usually the used solvent in the test solution

$$T = \frac{I}{I_0} \qquad (1)$$

Since the test compound is not present in the white point, the transmittance of the piece reference is defined as 100% of T.

$$\%T = \frac{I}{I_0} \times (100) \qquad (2)$$

In order to measure transmittance, a beam of light is aimed on the solution with certain intensity and wavelength, and the transmitted light across the cuvette containing the solution is measured. These techniques are within the spectrophotometry area, [15].

2.2.2 Opacity, [16], [17]**.**

It is the condition in which a matter prevents the passage of a light beam partially or totally. For that case, it is a derivative of the transmittance magnitude applied to environmental control. It is dimensionless and it is measured in a percentage scale. It is not recognized by the international system.

2.2.3 Spectrophotometer.

The spectrophotometer, figure 2, main function is to provide a radiant energy beam with a nominal wavelength and a bandwidth given. Any spectrophotometer spectral output used with a continuum source, regardless of its focal distance and slits width consists of a wavelengths range with an average length value that is presented on the spectrophotometer display, [18].

A spectrophotometer consists basically of:

- Entrance slit: It provides a narrow optical image of the radiation source.
- Lens collimator: it makes parallel the radiation from the entrance slit.

- Diffraction grating or prism: it disperses the incident radiation.
- Lens collimator 2: it reforms the images from entrance slit on the exit slit.
- Exit slit: it isolates the desired spectral band, blocking all scattered radiation except the desired range.

The secondary function of a spectrophotometer is energy adjustment efficiency. This can be increased by increasing the exit slit width, at the cost of increased spectral bandwidth that can introduce Beer's law deviations, because it requires monochromatic radiation [13].

Figure 2. Spectrophotometer used in the Fenix spectrophotometry Technology and Development Laboratory.
Source: UNICO S2150Spectrophoometer Series [19]

2.2.4 Opacimeter.

The opacity measurement has an important application in the environment, as it is referred to the evaluation of gases emission to the atmosphere from combustion of diesel in some vehicles traveling in the country. In the Automotive Diagnostic Centers the opacimeters are used as measuring instruments which must meet certain physical and optical characteristics. These requirements are explicitly presented in the 4231 NTC Standard. (*Paragraphs 2.34 Verification of linearity; 4.2.2 linearity; 4.2.9 neutral density filters*), [1].

Opacimeters are smoke analyzers of closed chamber operating under the procedure of sampling partial discharge. They have two measuring scales: One of them in light absorption units expressed in m^{-1} and the other one, linear, from 0% to 100% opacity. Both scales ranging from zero, the total light flux, up to the maximum scale value with complete obscuration, [20].

2. 3 Neutral density filters or certified reference materials (MRC)

The certified reference materials should be located in the beam path of light passing through the measurement area filled with air without opening the camera or using tools. The MRC in solid state allows the opacimeter routine evaluation on its correct operation through calibration and verification programs. The MRC optical properties should be of spectrally neutral optical density type, which allows a decrease in the wavelength significantly. The opacity values and light absorption coefficient, and its size, area of use and shape of the material and type of mounting depends on the design of each opacimeter manufacturer, thus the covered scope can not be very sweeping and usually the MRC is designed for a commercial trademark in instruments from other commercial trademarks and can not be used. Figure 3 shows transmittance spectra for various neutral optical density filters that sometimes opacimeter manufactors use as MRC and are called by the same reason as opacity filters. The conservation of the optical property of opacity filters depends on their surface quality; for this, contamination and deterioration of the surface during use, handling, transport and storage, should be avoided. [20].

2. 4 Technical regulations.

2.4.1 Colombian technique (Normative reference framework)

- **4231 Technical standard** *"Air Quality. Measurement procedure and characteristics of the partial flow equipment necessary for evaluating smoke emissions generated by diesel-powered mobile sources. Direct acceleration method"* [1].

Object: This standard is to establish the methodology to directly estimate the emission of particulate matter in the exhaust fumes of vehicles operating with diesel cycle, using the properties of light extinction that this issue presents. The methodology is developed under free acceleration conditions, which result is shared with the provisions of the current environmental regulations.

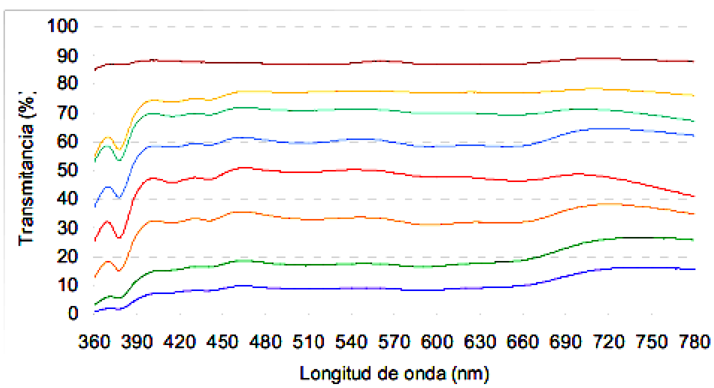

Figure 3. Neutral density lenses behavior in the visible light spectrum.

Source: CENAM Centro NACIONAL DE METROLOGÍA MEXICANA

Neutral density filters used in Colombia are shown in Figure 4.

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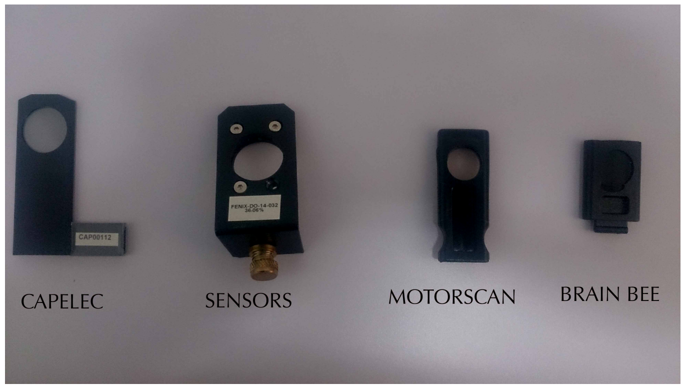

Figure 4. Neutral density filters marketed in Colombia.

Source: own.

- **17025 Technical standard "*General requirements for the competence of calibration and testing laboratories*",** [3].

  Object: This International Standard specifies the general requirements for the competence of testing and / or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods and methods developed by the laboratory itself.

2. 5 Calibration methods of ND neutral density filters.

2.5.1 Mexican method [21], [22], [23], [24].

The Mexican CENAM provides patterns for calibration of materials based on the recommendations of ASTM E275-93 and technical publications reference CNM-MFO-PT-001 and CNM-MFO-PT-002. These state a sweep in steps of 10 nm for all wavelengths of visible light spectrum without establishing a single true value and leaving the interpretation to the user. The procedure is coded as POC-UV-04; Spectrophotometrics UV-VIS Photometric scale filter measurements".

2.5.2 French method, [4].

The French method is established by the French Ministries Economy, Finance and Industry metrology branch; regarding the opacimeter construction mode, control and use. Under this method are set wavelength references for green light between 540 nm, and 590 nm. The result is the algebraic average of the above wavelengths and low uncertainty expressed by the calibration standards and the instrument references.

2.6 Validation materials and methods from spectrophotometry and metrology.

Fénix Technology and Development. FENIX-P-GC-020-4, developed a procedure for metrological assurance y FENIX-P-GC-021-2 for estimating uncertainty, [25], [26]. This consists of: robustness, repeatability, reproducibility, linearity, and uncertainty.

2. 6. 1 Robustness

Measurement condition within a set of conditions that includes different locations, operators, measuring systems and repeated measurements of the same objects or similar, [27]. The hypothesis to be tested in the ANOVA way of a factor is that population means are equal. The strategy to test the hypothesis of equal means is to obtain a statistical, called F, which reflects the degree of similarity between the compared measures, [28-32], [33]. Samples taken for analysis are shown on Table 1, and were obtained by the same operator in different work conditions. The variation factors correspond to the workstation situation: laboratory light and position of the entrance door position respect to the work area.

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3K023 Filter				90K023 Filter			
Closed Door Light Off				Closed Door Light Off			
n	1	2	3	n	1	2	3
% T	2,70	2,70	2,71	% T	90,82	90,83	90,81
Closed Door Light On				Closed Door Light On			
n	1	2	3	n	1	2	3
% T	2,71	2,71	2,71	% T	90,81	90,81	90,80
Open Door Light Off				Open Door Light Off			
n	1	2	3	n	1	2	3
% T	2,71	2,71	2,71	% T	90,82	90,81	90,81
Open Door Light On				Open Door Light On			
n	1	2	3	n	1	2	3
% T	2,71	2,71	2,71	% T	90,81	90,82	90,81

Table1. Collected Data for robustness test. 3k023 pattern filter.

Source: own.

Arithmetic average:

$$\overline{X} = \frac{n_1 + n_2 + n_3}{n} \qquad (3)$$

Groupal Media:

$$\overline{\overline{X}} = \frac{\overline{X}_1 + \overline{X}_2 + \overline{X}_3 + \overline{X}_4}{n} \qquad (4)$$

Variance:

$$S^2 = \frac{\sum\left(X_n - \overline{X}\right)}{(n-1)} \qquad (5)$$

Variance Group:

$$S_x^2 = \frac{\sum\left(\overline{X}_n - \overline{\overline{X}}\right)}{(n-1)} \qquad (6)$$

Joint or population variance:

$$s_p^2 = \frac{(n_1-1)s_1^2 + (n_2-1)s_2^2 + (n_3-1)s_3^2 + (n_4-1)s_4^2}{k(n-1)} = \sigma^2 \qquad (7)$$

Where k corresponds to the number of different conditions during data capture. Therefore,

$$k = 4 \qquad (8)$$

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Statistical Fisher calculated,

$$F = \frac{\sigma_1^2}{\sigma_2^2} = \frac{S_p^2}{\left(n \times S_x^2\right)} \qquad (9)$$

The critical statistical Fisher for this study is in tables and corresponds to [28, 29]:

(10)

Therefore:

$$F_{Calculated} < F_{Critic} \qquad (11)$$

Based on (11) it is confirmed that both the statistic calculated as the theoretical statistics are significantly equal. This ensures the robustness of method before the exposed disturbances of light and facilities for all the photometric scale.

2. 6. 2 Evaluation of repeatability and reproducibility.

2.6.2.1 Repeatability

Measurement condition within a set of conditions that includes the same measurement procedure, the same operators, the same measurement system, the same operating conditions and the same place and repeated measurements of the same object or similar object in a short period of time, [27].

2. 6. 3 Reproducibility:

Measurement condition within a set of conditions that includes different locations, operators, measuring systems and repeated measurements of the same object or similar objects, [27].

Within method validation it is one of the parameters to ensure the accuracy of the same. Precision depends only on the distribution of random errors and has no relation to the true value, [30]. The test was performed by taking 10 readings of each filter by the same operator and in a short period of time. The accuracy assessment is presented in Table 2.

Repeatability and reproducibility tests are performed directly, due to the method variations during its application are known. The laboratory does not apply its measurement in different equipments or alternative facilities. This determines that the only variable is the operator conditions change. Once done the analysis, it’s concluded *that there was no significant statistical difference and therefore the samples are equal and uniform.*

2. 6. 4 Linearity

It is the ability of an instrument or measurement method to provide an indication having a linear relationship with a different given magnitude of an influence quantity. Linearity is an important property of methods used to make measurements over a range of concentrations. The linearity of the response to pure standards of certified reference material (CRM). Linearity is not generally quantified, but is checked by inspection or using significance tests for non-linearity. The significant non-linearity is usually corrected by using nonlinear calibration functions or eliminated selecting an operating range. Any linearity residual deviation is normally counted by the estimated of the overall accuracy, covering several concentrations, or within any -associated with calibration- uncertainty, [31], [32], [33].

The equation of the line well given by (12),

$$y = mx + b \qquad (12)$$

Using the Table 2; develops the slope as,

$$m = \frac{\sum\left(x_i - \bar{x}\right)\left(y_i - \bar{y}\right)}{\sum\left(x_i - \bar{x}\right)^2} \qquad (13)$$

For the crossing point of the line have,

$$b = \left(\bar{y} - m\bar{x}\right) \tag{14}$$

Therefore, we have the equation of line defined in (15) as:

$$y = 1,0056697x - 0,0865843 \tag{15}$$

On the other hand, the substraction correlation can be found by:

$$r = \frac{\sum\left(x_i - \bar{x}\right)\left(y_i - \bar{x}\right)}{\sqrt{\sum\left(x_i - \bar{x}\right)^2 \sum\left(y_i - \bar{y}\right)^2}} \qquad \textbf{(16)}$$

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3K023					
Operators	Op 1	Op 2	Op 1	Op 2	Op 1
Time	Day 1	Day 2	Day 3	Day 4	Day 5
1	2,74	2,76	2,74	2,75	2,74
2	2,74	2,76	2,74	2,75	2,74
3	2,75	2,76	2,75	2,74	2,74
4	2,75	2,76	2,75	2,76	2,74
5	2,75	2,76	2,75	2,75	2,74
$\bar{X}$ =	2,75	2,76	2,75	2,75	2,74
$\bar{\bar{X}}$	2,75				
S^2	0,00003	0,00000	0,00003	0,00005	0,00000
S =	0,006	0,000	0,006	0,007	0,000
S_r^2 =	0,00002				
S_L^2 =	0,00005				
S_R^2 =	0,00008				

10K023					
Operators	Op 1	Op 2	Op 1	Op 2	Op 1
Time	Day 1	Day 2	Day 3	Day 4	Day 5
1	9,07	9,09	9,07	9,10	9,05
2	9,07	9,09	9,07	9,10	9,05
3	9,08	9,09	9,07	9,10	9,05
4	9,08	9,09	9,07	9,10	9,05
5	9,08	9,09	9,07	9,10	9,06
$\bar{X}$ =	9,08	9,09	9,07	9,10	9,06
$\bar{\bar{X}}$	9,08				
S^2	0,00003	0,00000	0,00000	0,00000	0,00002
S =	0,006	0,000	0,000	0,000	0,005
S_r^2 =	0,00001				
S_L^2 =	0,00035				
S_R^2 =	0,00036				

50K044					
Operator	Op 1	Op 2	Op 1	Op 2	Op 1
Time	Day 1	Day 2	Day 3	Day 4	Day 5
1	45,33	45,36	45,32	45,39	45,34
2	45,33	45,36	45,33	45,39	45,34
3	45,34	45,36	45,33	45,39	45,34
4	45,34	45,37	45,33	45,39	45,34
5	45,34	45,37	45,33	45,39	45,35
$\bar{X}$ =	45,34	45,36	45,33	45,39	45,34
$\bar{\bar{X}}$	45,35				
S^2	0,00003	0,00003	0,00002	0,00000	0,00002
S =	0,005	0,005	0,004	0,000	0,004
S_r^2 =	0,00002				
S_L^2 =	0,00063				
S_R^2 =	0,00065				

90K023					
Operator	Op 1	Op 2	Op 1	Op 2	Op 1
Time	Day 1	Day 2	Day 3	Day 4	Day 5
1	91,41	91,40	91,39	91,42	91,42
2	91,41	91,39	91,39	91,42	91,41
3	91,41	91,39	91,38	91,42	91,42
4	91,40	91,39	91,40	91,44	91,42
5	91,41	91,39	91,39	91,42	91,42
$\bar{X}$ =	91,41	91,39	91,39	91,42	91,42
$\bar{\bar{X}}$	91,41				
S^2	0,00002	0,00002	0,00005	0,00008	0,00002
S =	0,004	0,004	0,007	0,009	0,004
S_r^2 =	0,00004				
S_L^2 =	0,00022				
S_R^2 =	0,00026				

Table2. Repeatability and reproducibility Evaluation. Source: own.f

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	LECTURAS	PATRON
LENTE	y	x
3K023	2,71	2,77
10K023	8,98	9,10
50K044	45,39	45,43
90K023	91,41	91,45
$\overline{X}$ =	37,1220	37,1875

Table 3. Datas for calculating the linearity of the method. Source: own.

To define the linearity *student t* test is used as follows (table 3): [34]

To find the t statistic calculated, it is applied: (17)

$$t = \frac{|r|\sqrt{(n-2)}}{\sqrt{(1-r^2)}} \tag{17}$$

From the Student's t tables, this statistical test is got [38] as,

$$t = 4,30265273 \tag{18}$$

And, as test conclusion it is obtained:

$$\begin{gathered} t \geq t_{crítico} \\ 153,62 > 4,30265273 \end{gathered} \tag{19}$$

Therefore, there is correlation to the method.

2. 6. 5 Uncertainty budget, [26], [35].

As a requirement for laboratory accreditation, the method should be brought under standards of their uncertainty calculations. Table 4 and Table 5.

The estimation of the uncertainty is in principle a simple process. The steps involved in the process of estimate and evaluation of measurement uncertainty can be summarized as follows, [36]:

1. Establishment of the measurand.

2. Identification of uncertainty sources.
3. Quantifying uncertainty components.
4. Calculation of the combined and expanded uncertainty.

UNCERTANTY BUDGET														
wl	TRANSMITTANCE			$\bar{x}$	STANDARD DEVIATION	UNCERTAINTY FOR REPEATABILITY	UNCERTAINTY CERTIFIED PATTERN	COVERAGE FACTOR	U PATTERN	RESOLUTION	U RESOLUTION	U COMBINED	COVERAGE FACTOR	U EXPANDED
nm	1	2	3	T%	S	U	Up	K		T%	Ur	Uc	K	Uex
540	80,71	80,72	80,72	80,72	0,00471	0,00272	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42
545	80,76	80,76	80,74	80,75	0,00943	0,00544	0,42	2	0,21	0,01	0,00289	0,2101	2	0,42
550	80,73	80,73	80,73	80,73	0,00000	0,00000	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42
555	80,61	80,62	80,62	80,62	0,00471	0,00272	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42
560	80,43	80,44	80,43	80,43	0,00471	0,00272	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42
565	80,18	80,19	80,17	80,18	0,00816	0,00471	0,42	2	0,21	0,01	0,00289	0,2101	2	0,42
570	79,89	79,88	79,87	79,88	0,00816	0,00471	0,42	2	0,21	0,01	0,00289	0,2101	2	0,42
575	79,56	79,55	79,55	79,55	0,00471	0,00272	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42
580	79,21	79,22	79,26	79,23	0,02160	0,01247	0,42	2	0,21	0,01	0,00289	0,2104	2	0,42
585	78,97	78,99	79,00	78,99	0,01247	0,00720	0,42	2	0,21	0,01	0,00289	0,2101	2	0,42
590	78,84	78,84	78,85	78,84	0,00471	0,00272	0,42	2	0,21	0,01	0,00289	0,2100	2	0,42

Table 4. Uncertainty Budget. Source: own.

Nº	MAGNITUDE OF ENTRY XG	INFORMATION SOURCES	ORIGINAL UNCERTAINTY	TYPE OF DISTRIBUTION	STANDARD UNCERTAINTY U (XG)	SENSITIVITY COEFFICIENT	PERCENTAGE OF IMPACT
1	REPEATABILITY	REPEATER MEASUREMENTS	0,00272	A NORMAL	0,00272	1	0,016770%
2	RESOLUTION SPECTROPHOTOMETER	SPECIFICATIONS OF THE EQUIPMENT	0,001	B RECTANGULAR	0,00289	1	0,018932%
3	CALIBRATION SPECTROPHOTOMETER	CALIBRATION CERTIFICATE	0,42	B NORMAL	0,21	1	99,964297%
EXPANDED UNCERTAINTY						0,42000749	
COMBINED UNCERTAINTY						0,210037498	
COVERAGE FACTOR FOR 95% OF CONFIDENCE						2	

Table 5. Parameters of method total uncertainty. Source: own.

2. 7 Analysis and design of calibration software for opacity lens.

2.7.1 Software design and Overview.

Based on the S-2150 SERIES SPECTROPHOTOMTER USER'S MANUAL V 2.0, [37], Operation Manual, the *K3 Analysys spectrophotometry View 2.3*, low-level software establishes a communication between the UNICO 2150 Spectrophotometer and the lab main computer of by Delphi development environment version 2014. The database engine belongs to Interbase / Firebird. It was designed a simple and friendly graphical environment, in order to be operated by the metrologist and laboratory chief under a previous training by the laboratory and authors. The

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software complies with the security restrictions and data encryption as required by the 17025 NTC Colombian technical standard (Paragraph 5.4.7 Data Control), [3].

The software allows the storage of all the tests conducted by the team worked with Interbase on a data base. It stores test data such as date, time, average in all wavelengths, uncertainty, variance, expanded uncertainty. In addition, data stored customer information and reference material such as serial, NIT or certificate, client, address, telephone and city.

2.7.2 Application start

The income to software is done by 2150 icon. To Protect Customer Data the NTC Standard 17025 requires the operator identification handling such data. This requirement is authenticated by passwords requirement. A password exists for a metrologist and a different one for the laboratory manager.

2.7.3 Main screen

Once inside the application, the software will cast the main screen where you can revise previous tests, previous calibrations or make a new certification test. It is also possible to check the spectrophotometer serial, software version and name. (Figure 6)

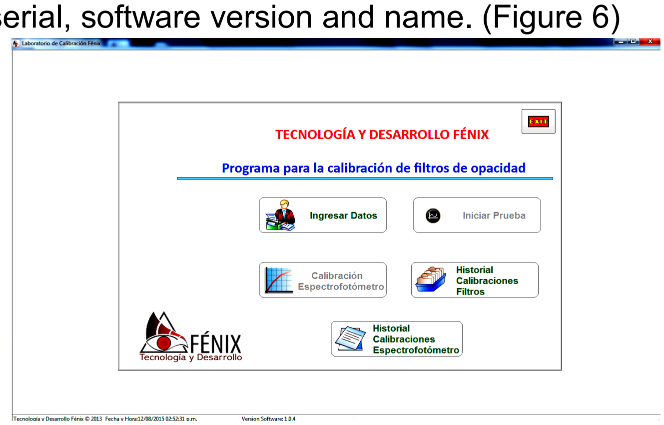

Figure 6. Main Menu. Source: own.

2.7.4 Data entry

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To start a certification test, customer data must be entered. Once data have been entered, the software will guide the user towards the identification of the reference material. There, it will require the filter brand data and serial identification the one which we want to register the calibration registry with. Figure 7. In this same block, it is registered a material photography to be stored by their status at the time of calibration.

2.7.5 Start of calibration test.

Once stored all data regarding the customer identification and reference material, the button "Start Test" software synchronizes the spectrophotometer communication with the receiving data of the computer communication port. The friendliness of the software guides the operator throughout the test calibration, requesting the suitable test conditions during the process.

This is how the software will perform three sequences of the way described below and based on No. 98.00.852.005.1. Circular. The software positions the spectrophotometer wavelength at 535 nm length and sweeps to the wavelength of 590 nm, increasing in steps of 5 nm.

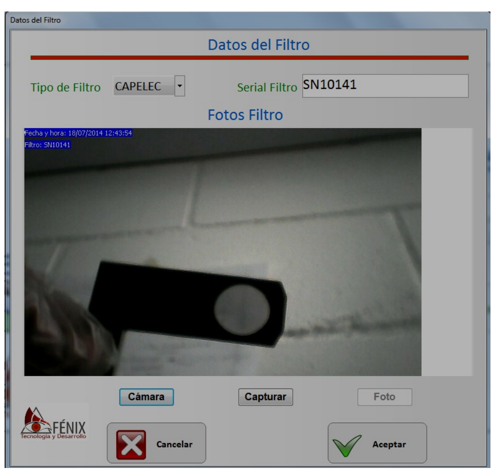

Figure 7. Reference material identification. Source: own

For each sequence, the device performs a bleaching event to eliminate parasitic currents and Pre-scrutinize the equipment.

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After the reset of all wavelengths related to the method, it is proceded to capture quantitative results of transmittance for each wavelength as shown in Figure 8. The software stores each datum and when the third sequence of full shots ends, proceed to perform the calculations of average, variance, fashion and implements the budget of uncertainty described in 2.4 After these calculations the software generates a calibration report.

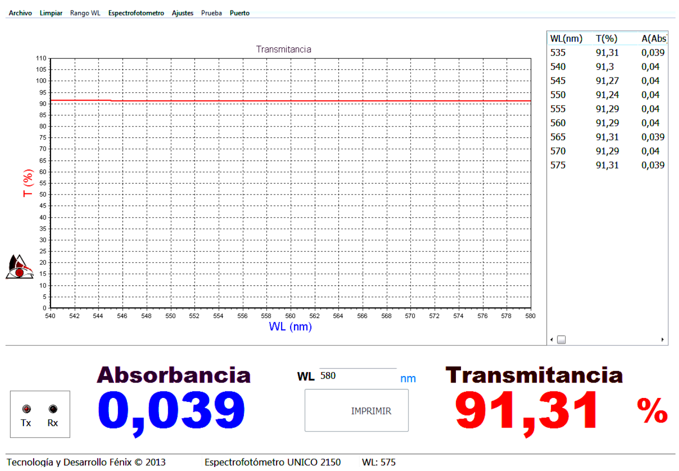

Figure 8. Transmittance data registration. Calibration test. Source: own

2.7.6 Calibration certificate.

The laboratory generates a calibration certificate which has the required architecture by the 17025 NTC to calibration certificates issue in its item 5*.10.2 Test reports and calibration certificates architecture. 5.10.4 Calibration certificates*, [3]. The printed information is as required by the 17025 NTC.

3. Results

During the software implementation communication, problems with the termohigrómetro communication port speed were presented. As a result, they had to change the communication

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speed of the communication port and the problem was solved. Weekly control tests on measuring patterns are performed. There, statistical calculations were performed and testing procedures checking that the method, the patterns and the instrument are in the metrological capability to perform calibrations and / or measurements. Within the sturdiness of the method were created eventualities as testing abortions, power failures, disconnection of termohigrómetro, bad connection of communication port of spectrophotometer and the results did not yield any data loss.

When subjected to internal audits and external audits, the software responded optimally and has not been the subject of criticism by specialists. The software has been evaluated by the ONAC (Organismo Nacional de acreditación) and the INM (Instituto Nacional de Metrología) casting a good impression before the reviewers due to this is the first validated and automated calibration software in Colombia.

In addition, validation of the method has not been completed to the satisfaction for certification bodies. Bias test validation, control charts, truthfulness, anomalous data analysis is still required. The reproducibility requires to be tested for primary order and for that, it is necessary for other spectrophotometry equipment. For delivery date of this document, the instrument was in acquisition process. However the validation software has not shown any problem for the auditors and international experts who have seen their performance *in situ*.

By analyzing the database stored results, the internal audits and management reviews have been carried out smoothly. Applications for complaints, claims, nonconforming work and certificate copy issuance, works properly under the search engine and no error has occurred and / or loss of information of the dated up today tests. The software fully complies with the requirements by the 17025 NTC. At this time the software is in version 3.0 waiting improvements required by Laboratory Head.

By August 1st, 2015, calibrations had been made 450 calibrations of lens calibration for laboratories, diagnostic centers and private clients. Furthermore, 984 control tests have been performed, intermediate checks, tracking of patterns measurements of photometric scale and scale wavelength.

Correction works have been carried out and and curve fitting, depending on the material of materials certification value. On the other hand, a photography storage problem has been identified. As the number serial has more than 14 characters, photography could not be read by the software. However, no loss of information was present and by expanding the storage registry, the committed photography serials were recovered.

4. Conclusions.

- The software calibration for neutral density lens of FENIX TYD spectrometry laboratory fully complies with the standards set forth in 17025 NTC for testing and calibration laboratory. Similarly, the software and validated method complies with the requirements in the 4231 NTC technical standards.
- The calibration software works based on the French *Circular No. 98.00.852.005.1* from the Economy, Finance and Industry French Ministry, Metrology Branch. It has been reviewed and approved by the regulatory body of the country scientific metrology INM and by the regulatory body accreditation of laboratories Colombians, ONAC, based on standards issued by the regulatory body of legal metrology of Colombia ICONTEC.

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- Although it has not achieved laboratory accreditation, the INM and the ONAC have not considered the software as a non-compliance or point to be taken into account in its audits. The delay in the accreditation passes through an ignorance topic of the transmittance magnitude. At this time, Colombia does not have any technical expert who can evaluate metrologically the TYD FENIX laboratory statistical study. Therefore, the laboratory has found it necessary to contact international experts and laboratories abroad in order to try to make an inter laboratory in the future and compare the method implemented and described herein.
- By taking implemented and created standards in another country, usually not necessary to demonstrate the method, since it is already validated by the creators. However, this move is not internationally standardized despite being endorsed by the French government and approved by the Committee français d'accréditation COFRAC.
- Create a measurement method and validate it from scratch, it requires further investigation, study materials, response equipment, statistical analysis, physicochemical analysis and much more investment. Therefore, the TYD Phoenix Laboratory found in the French method implementation the perfect solution to the metrological vacuum in the country at this time.
- Importantly, the methods of metrological validation of magnitudes such as temperature, weight, length, time etc., are nothing close to the methods used for analyzing the magnitude of transmittance. Therefore, when auditing the study presented in the paper, it is absolutely necessary to be performed by an expert technician with experience in the area. Otherwise, there can be properly evaluated.

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- To Patent the method in our country is possible, but is not the policy of metrology that is intended to implement in the country. The concept goes through a universal metrology open to change and not segregate to schools or entities that do not allow the development potential and better methods.
- The Phoenix TYD Laboratory wants to generate recognition in this method in technological innovation in the country. Responsible for generating this recognition is the National Metrology Institute (NMI), but now is not a priority for the INM because its spectrophotometry department is developing and does not have yet the knowledge and experience to assess the subject.
- To validate the method it is necessary to make the respective truthfulness studies, bias and traceability that are not described in the document but they were made. However at the time of the audit validation criteria they were not ready. Which generated a nonconformity by specialists.

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The product of this project is Intellectual Property of TYD Phoenix Spectrometry Laboratory. Source code and software programming are covered by the Special Unit of the National Directorate of Copyright of the Ministry of Interior of Colombia. This document is part of the final product of the GIRMA Research Group in conjunction with Phoenix Technology and Development Company S.A.

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