INTERNATIONAL STANDARD TEST METHOD FOR DETERMINATION OF ALKALINITY CONTENT IN NATURAL RUBBER LATEX CONCENTRATE

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ABSTRACT

This paper discussed the work done by the Malaysian Rubber Board (MRB) in revising the standard test method applicable to rubber and rubber products internationally. In 2016, the ISO technical committee elected Malaysia, represented by the MRB as the project leader for revision work of ISO 125:2011 - Determination of alkalinity content in natural rubber latex concentrate. The main goal of this project is to revise ISO standard test method (ISO 125:2011) by establishment of proper procedures for standardisation of sulfuric and hydrochloric acid in titration process. This paper also specifically discussed the comparison study between sulfuric acid and hydrochloric acid using two titration techniques, namely potentiometric and visual indicator. The results obtained were evaluated using statistical analysis which demonstrated comparable results between both acids and titration methods. Reliable precision statement in terms of repeatability (r) and reproducibility (R) was generated through the Interlaboratory Testing Programme (ITP). Hence, a new comprehensive precision statement for the test method was successfully established. The new edition of ISO 125:2020 was successfully published in February 2020. This project enhances the image and credibility of the MRB, especially at the national and international levels as an expert body in the development of standard test methods for natural rubber (NR) latex concentrate.

Keywords: standard test method, alkalinity, standardisation, precision

INTRODUCTION

A standard is a technical document designed to be used as a rule, guideline or definition that provides requirements, specifications or characteristics and is reviewed in terms of its technical content and presentation to ensure that the content is valid, accessible and appropriate to the current technology advancement, that can be used consistently to ensure that materials, products, processes and services are fit for their purpose (Ratna Sari Dewi *et al*., 2021). Standards have been practised in most aspects of our daily life. For example, the standardisation in chemical testing sector promotes best industry practices that emphasise safety and quality control.

Standards are a recognition of product quality and intended to meet market needs, which can provide people and organisations with a basis for mutual understanding and are used as a tool to facilitate communication, measurement, trade and manufacturing. According to Zhang *et al*., 2019, there are three main characteristics of standards that can affect the economic growth which are consistency, compliance and compatibility. These three characteristics would enable products to be consistent with requirements and gain market recognition.

International Organization for Standardization (ISO) is an independent, non-governmental international organisation consisting of national standards bodies. This organisation is responsible to develop and publish technical, industrial and commercial standards worldwide. Experts from all over the world work together, share their knowledge and develop voluntary, consensus-based decisions. In other words, the ISO standards are internationally agreed by them. As mentioned by Kartini *et al*., 2017, the ISO test methods need to be revised once in five years to cater to any new technologies and improvement in the methodologies. The introduction of additional or alternative techniques is needed for wider acceptance of the test methods. The revision work, which was done through standardisation activities (ISO/IEC Guide 2, 2004), will provide current information and latest precision statement to the revised test methods which are being referred to by the rubber industry, both nationally and internationally.

Development of International Standards

The MRB is responsible in ensuring that national positions are obtained with regards to the development of international standards and related issues of ISO/TC 45 and its sub-committees. These tasks are managed through the relevant national mirror committees under the MRB's management. The task also includes casting Malaysia's vote into the ISO online system for balloting (Farinie *et al*., 2017). The standards may be used as a tool for marketing and to streamline the whole industry for a fair competition. The MRB needs to ensure that only standards with clear market demands and needed by the industry are developed. The MRB has significantly contributed to the development of the rubber industry for the past decades through its excellence in research and development and technical services (Norlee *et al*., 2018). This is an advantage for the MRB in identifying and prioritising standards development that can generate maximum value for the industry.

MRB involvement in the standardisation activities

The MRB through the Department of Standards Malaysia (DSM), has been actively involved in national, regional and international standardisation activities, particularly in rubber related committees. Standards are a recognition of a product quality and intended

to meet market needs. Moreover, standards that are widely accepted can be used to support mutual recognition arrangement (MRA), provide trade facilitation as well as elimination of trade barriers, both regionally and globally (Norlee *et al*., 2018 and Kartini *et al*., 2017). A standard is reviewed in terms of its technical content to ensure that the content is appropriate to the latest technology and pratices. In addition, the standard may be revised, amended, confirmed or withdrawn as an outcome of the annual systematic review.

Through active participation as a project leader or as a subject matter expert, the MRB is responsible to develop and revise ISO standard related to both rubber and rubber products. The scope covers standardisation of terms and definitions, test methods and specifications (ISO/IEC Guide 2, 2004) for rubber products. The proposals for the development of a new ISO or revision work are reviewed and developed in a transparent manner and that consensus is achieved among the Standards Development Committee. The published ISO are systematically reviewed by the working groups of each technical committee every five years (Farinie *et al.*, 2017 and and Kartini *et al*., 2017). The structure of documents for ISO standards are drafted in a uniformed and practical manner, irrespective of technical contents. It shall follow the guidelines on the presentation of Malaysian Standards as specified by Standards Malaysia (Farinie *et al.*, 2017).

In general, the revision allows for the insertion of a new test method into the current standards to widen its acceptance due to the advancement of technology. Currently, most of the MRB chemical testings in rubber and rubber products have become a global source of reference to those involved in the rubber industry (Norlee *et al*., 2018). This indicates that the MRB is one of the experts in the field of rubber and rubber products testings. Thus, it has become an important task for the MRB to lead the revision work in safeguarding the interests of the Malaysian rubber industry (Kartini *et al*., 2017). The MRB has continued to contribute towards the publication of national and international standards through continuous efforts in method development and standardisation works.

Natural rubber latex

Natural rubber is produced by about 2500 plant species, many of which are of tropical origin (Bowers, 1990). However, all commercially available NR is harvested from a single species, *Hevea brasiliensis* (Bonner and Galston, 1947 and Blackley, 1997). Over the years, NR is mainly used in many applications and products, either by itself or in mixture form with other materials. In most of its useful forms, it has a large stretch ratio and high resilience and is extremely waterproof. In general, NR latex is a stable colloidal dispersion of polymeric materials (latex particles) in an aqueous medium (Blackley, 1997).

NR latex contains polymers of the organic compound isoprene with insignificant amount of impurities of other organic compounds and water. The structures of polyisoprene that are used as NR are classified as elastomers (Blackley, 1997). These elastomers, in the form of milky white sticky emulsion colloid, undergo the state changes from liquid to solid for commercial processing. The rubber particles that consist of elastomers make up to about 30% w/v of fresh latex, whereas most of non-rubber constituents are either dispersed or dissolved in the latex serum (Blackley, 1997). Freshly-tapped NR latex is a sticky, whitish fluid with a density in the range of 0.97 – 0.98 g cm^{-3} as well as pH ranged in between 6.0 and 7.0 and surface-free energy with variable viscosity that varies over a considerable range (Bonner and Galston, 1947). The particles are generally spherical, although pear-shaped particles might be observed in mature trees.

As the latex is a natural product, its composition varies and typical composition is given in Table 1 (Blackley, 1997).

Table 1. Typical composition of fresh natural rubber

Components	Proportion (wt% on whole latex)
Total solids	36
Dry rubber	33
Proteinaceous substances	1 – 1.5
Resinous substances	1 – 2.5
Ash	Up to 1
Sugars	1
Water	Around 60

Since NR is the sap of *Hevea brasiliensis*, it contains not only rubber but also proteins, lipids and other materials. Due to this, chemical changes occur to the latex shortly after it leaves the tree (Blackley, 1997). The chemical changes results in the coagulation of latex and development of bad odours. Natural rubber latex undergoes spontaneous or natural coagulation within a few hours after tapping, due to bacteria and enzymic actions on the non-rubber constituents. This results in the developments of acidity and destabilisation of the latex through microorganisms interactions with various non-rubber constituents (Blackley, 1997).

Ammonia as preservation

Preservation and stabilisation through chemical incorporation into the latex are crucial in the processing of NR latex. These chemicals should kill and inhibit the activity of latex microorganisms, maintain or enhance the colloid stability of the latex and deactivate trace metal-ions as mentioned by Santipanusopon and Rijayan, 2009. Generally, five chemicals are commonly used in preservation system to stabilise the latex in fluid state *i.e.* ammonia, potassium hydroxide, formaldehyde, sodium sulphite and boric acid.

As reported by Narongwongwattana *et al*., 2015, most rubber factories monitor ammonia content or alkalinity during processing and storage as it is an important parameter. Ammonia also plays an important role in enhancing the colloid stability of the latex. It causes the bottom fraction to dissolve in the aqueous phase of the latex. The dissolution is assisted by slow hydrolysis of the proteins and lipids into polypeptides, amino acids, glycerol, long chain carboxylate anions, phosphate anions and organic bases (Blackley, 1997). The hydrolysed species later adsorb onto the surface of the rubber particles, thereby enhancing its colloid stability.

Ammonia is a very active bactericide which retards the activity of volatile fatty acids (formic acid, acetic acid and propionic acid) produced through the interaction of microorganisms with various non-rubber constituents in the latex (Lowe, 1960 and Blackley, 1997). In most previous and currently developed preservation systems, ammonia is still widely applied, for both short (0.2 wt% on whole latex) and long term (0.7 wt% on whole latex) preservation systems. The use of ammonia as preservative can help overcome this scenario since ammonia can inhibit bacterial action and growth, subsequently keep the field latex in liquid form (Subramaniam, 1989).

Other benefits of ammonia are the deactivation of magnesium ions in the latex through formation of magnesium ammonium phosphate, being less harmful to people, having no effect on the rubber particles and imparting no colour to the latex (Santipanusopon and Rijayan, 2009). However, the ammonia content needs to be kept as low as possible because high proportion of ammonia in skim latex will contribute to high acid consumption in skim coagulation and environmental pollution. Major disadvantages of ammonia, apart from imparting strong odour is that it interferes with some established latex processes and causes problem to the environment (Blackley, 1997). The ammonia affects the environment through the nitrogen cycle. Large quantities of ammonia discharged through latex processing into the environment can cause harm to aquatic life, plants, livestock, air and soil. Blackley, 1997, has found that the addition of excess ammonia in NR field latex has resulted the high gel content in latex due to the formation of zinc-amine complex under heat condition.

Field latex and latex concentrate

Field latex is a latex freshly-tapped from trees which is slightly alkaline or neutral. It will become acidic due to bacterial action which produce various organic acids such as asetic acid and propionic acid. As a result, the formation of organic acids neutralises the negative charge on rubber particles and causes the latex to coagulate (Blackley, 1997). Therefore, fresh latex cannot be kept for long without preservative treatment. The field latex tends to coagulate and become unsuitable for the production of latex concentrate. The instability is due to several reasons such as the increase of volatile fatty acid (VFA) number, the presence of foreign materials and chemical reaction (Lowe, 1960). The NR field latex serum is an ideal medium for bacteria growth. This leads to bacterial attack and thus, double the number of VFA especially in unpreserved field latex.

Natural rubber latex concentrate, also known as centrifuged latex, is obtained by centrifugation and is preserved with high amount of diammonium hydrogen phosphate. It is the most common grade of latex used worldwide. It gives excellent films of high clarity and has good adhesion characteristics as a binding agent when suitably compounded (Panmanas and Chin, 2019). The compounded latex has wide applications especially in dipped products such as medical and industrial gloves, household gloves, rubber threads, balloons, condoms, catheters and other applications (Mohd Afieq and Rosmahani, 2017).

MATERIALS AND METHODS

According to Blackley, 1997, the term of alkalinity refers to the total alkaline in latex. Since ammonia is commonly used as anticoagulant for latex, the term is now often used to express the amount of ammonia added in the latex. In this experiment, a test portion of NR latex concentrate was titrated with acid to pH 6.00 ± 0.05 in the presence of a stabiliser (5% solution of non-ionic stabiliser of the alkyl phenol polyethylene oxide condensate) to prevent coagulation either by electrometrically (potentiometric titration) or with methyl red as a visual indicator. The alkalinity is calculated from the quantity of acid required as specified in ISO 125:2020. The amount of ammonia in latex can be determined titrimetrically using either 0.05 mole/dm^3 sulfuric acid with methyl red as an indicator or by titration using 0.1 mole/dm^3 of hydrochloric acid. For ammonia-preserved latex, the alkalinity is expressed as the amount of ammonia in 100g of water in the latex.

As specified in the ISO 125:2020 standard test method, the alkalinity content (as NH_3), A_{NH3}, is expressed as the percentage (by mass) of ammonia (NH_3) in the latex concentrate calculated using the following formula:

$$A_{NH3} = \frac{F_1\, c\, V}{m}$$

Where:

F_1	is a factor: 1.7 for hydrochloric acid or 3.4 for sulfuric acid
c	is the actual concentration, expressed in moles of HCl or H_2SO_4 per cubic decimetre of acid used
V	is the volume of acid used, in cubic centimetres
m	is the mass of the test portion, in grams

The result was reported as the mean of the duplicate determinations.

Standardisation of 0.05 mol/dm^3 sulfuric acid and 0.1 mol/dm^3 hydrocloric acid

Standardisation is the process of determining the exact concentration (molarity) of a solution. Titration is an analytical procedure often used in standardisation. In a titration, an exact volume of one substance is reacted with a known amount of another substance and the point at which the reaction completes is referred to as the end point. A chemical substance known as colour indicator is typically used to indicate the end point. In the standardisation of acid-base by titration methods, a colour indicator, namely methyl orange is usually selected due to its clear and distinct colour variance at different pH values. In acidic medium, methyl orange shows red colour while in basic medium, it shows yellow colour. If a solution becomes less acidic, methyl orange changes from red to orange and finally to yellow with the reverse process occurring in a solution of increasing acidity (Chairunisa and Imawan, 2019 and Patricia *et al.*, 2010).

In this standardisation procedure of two acids namely 0.05 mol/dm^3 sulfuric acid (H_2SO_4); approximately 10 ml of 0.05 mol/dm^3 Na_2CO_3 was used to stardardise the 0.05 mol/dm^3 H_2SO_4. A few drops of methyl orange were added to the solution as an indicator which provides colour changes when the end point (or equivalence point) is reached. On the other hand, for the standardisation of 0.1 mol/dm^3 HCl, approximately 10 ml of 0.05 mole/dm^3 Na_2CO_3 was used to stardardise the 0.1 mol/dm^3 HCl using methyl orange as an indicator.

By determining how much of the Na_2CO_3 solution is required to neutralise both 0.05 mol/dm^3 H_2SO_4 and 0.1 mol/dm^3 HCl, a value for concentration of both acids can be measured accurately by means of titration process. Due to the nature of Na_2CO_3 which is hygroscopic and could absorb moisture from atmosphere, thus it is important to dry the Na_2CO_3 at 120 ºC ± 5 ºC for 2 hours before preparing 0.05 mol/dm^3 solution.

RESULTS AND DISCUSSION

Comparison results between sulfuric acid and hydrochloric acid

The comparison studies between two types of acids namely sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were conducted and the findings were discussed. For experimental procedures and sample materials, highly ammoniated (HA) latex concentrate sample obtained from Sime Darby, Batu Anam in Segamat, Johor was titrated to pH 6.0 ± 0.05 by potentiometric titration in the presence of a non–ionic stabiliser and its alkalinity is calculated from the quantity of acid required (Mohd Afieq and Muhammad Nor Syafwan, 2019). The data obtained from both acids were analysed and evaluated using statistical analysis of F-test and t-test.

Table 1. Comparison results between sulfuric acid and hydrochloric acid

Sample Reference	Mean of NH_3 (%)	
	H_2SO_4	HCl
HA-1	0.60	0.59
HA-2	0.60	0.61
HA-3	0.60	0.61
HA-4	0.60	0.60
HA-5	0.59	0.60
HA-6	0.59	0.60
HA-7	0.60	0.59
HA-8	0.60	0.61
HA-9	0.60	0.61
HA-10	0.60	0.60
HA-11	0.59	0.60
HA-12	0.59	0.60
HA-13	0.60	0.61
HA-14	0.61	0.60
HA-15	0.61	0.60
HA-16	0.59	0.60
HA-17	0.59	0.60
HA-18	0.59	0.60

average	0.60	0.60
sd	0.0067	0.0062
%CV	1.12	1.03
min	0.59	0.59
max	0.61	0.61

Figure 1. Sulfuric Acid vs Hydrochloric Acid

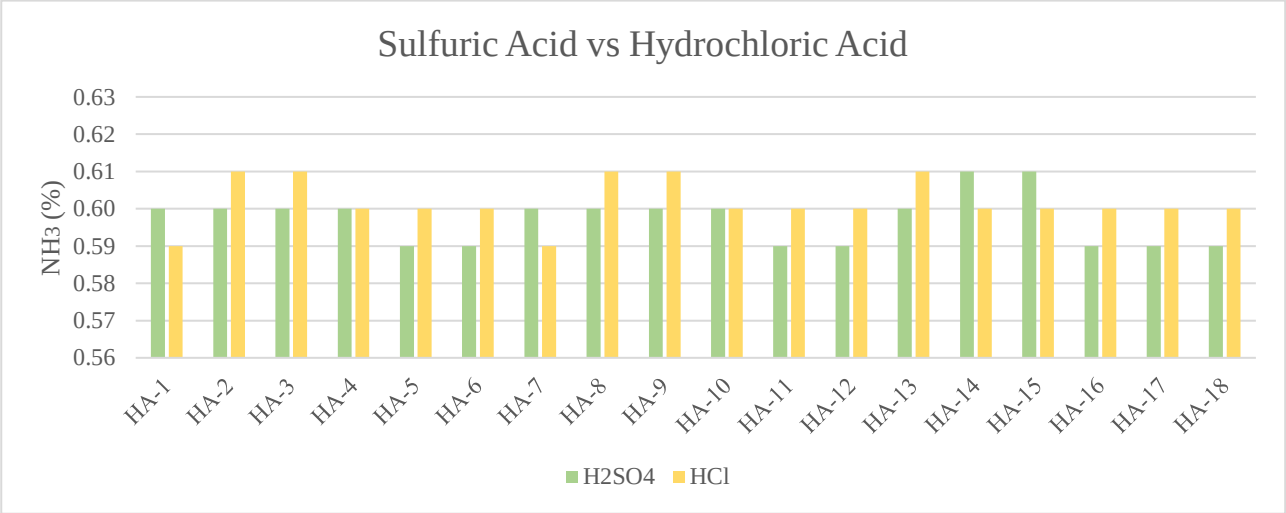

Table 2. Summary of F-test and t-test

Statistical Parameter	Value
F calculated	1.10
F critical	2.31
P value	0.06
t statistic/calculated	-2.06
t critical	2.04

Figure 1 shows the overall performance of H_2SO_4 and HCl. As shown in Table 1, the average differences between coefficients of variation (CV) obtained by using both acids were 0.1% in which the trend showed that H_2SO_4 was slightly higher compared to that of HCl. The average mean values of $\%NH_3$ produced by both H_2SO_4 and HCl is similar, ranged between 0.59 to 0.61. As shown in Table 2, p-value (0.06) recorded more than $\alpha = 0.05$ (standard significance level, 95% confidence level), and the data was further analysed by using t-test method to assess the significant difference of the mean value between H_2SO_4 and HCl. As indicated in Table 2, the F-calculated (1.10) is less than F-critical (2.31) and t-statistic is less than t-critical. Thus, it was observed that there is no significant difference in mean of $\%NH_3$ obtained for both acids. Therefore, it is concluded that both H_2SO_4 and HCl can produce comparable results.

Potentiometric titration vs visual indicator (sulfuric acid)

The study aimed to evaluate the performance of two different titration methods. In this work, H_2SO_4 was chosen and both titration methods of potentiometric titration and visual indicator were performed and analysed simultaneously following the ISO 125 test procedure. As shown in Table 3, the average values for both titration methods recorded was 0.60. The visual indicator titration showed higher CV with 2.32% compared to potentiometric titration (CV = 0.87%) which indicated that potentiometric titration is more precise. The overall mean values of $\%NH_3$ produced by potentiometric titration ranged from 0.59 to 0.60 while for visual indicator, titration ranged from 0.58 to 0.61.

Table 3. Comparison results between potentiometric titration vs visual indicator

Titration Method (H_2SO_4)	Mean of NH_3 (%)	
	Potentiometric	Visual Indicator
HA-1	0.60	0.60
HA-2	0.60	0.61
HA-3	0.60	0.61
HA-4	0.60	0.59
HA-5	0.59	0.58
HA-6	0.59	0.58
average	0.60	0.60
sd	0.0052	0.0138
%CV	0.87	2.32
min	0.59	0.58
max	0.60	0.61

Figure 2. Potentiometric titration vs visual indicator (sulfuric acid)

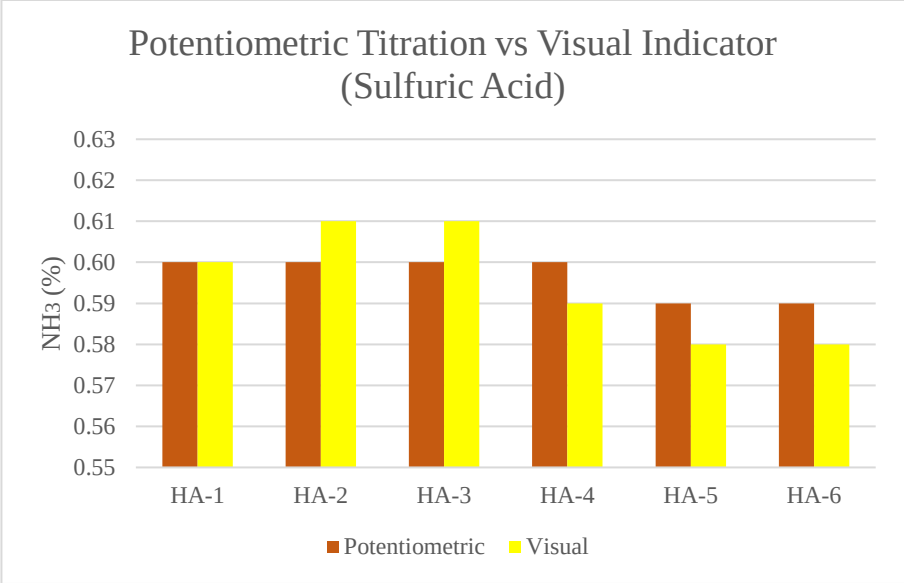

Table 4. Summary of F-test and t-test

Statistical Parameter	Value
F calculated	0.14
F critical	0.19
P value	0.39
t statistic/calculated	0.27
t critical	2.44

The overall performance of both titration methods was illustrated in Figure 2. Statistical analysis of F-test and t-test were conducted to reveal if there were significant differences in the mean of NH_3 by both potentiometric and visual indicator titration (Table 4). As observed, the p-value (0.39) recorded is more than $\alpha = 0.05$ which indicated an interaction between measurement, thus the data was further analysed by using t-test to assess the significant difference of the mean value between potentiometric and visual indicator titration. The outcome showed that there was no statistically significant difference between the two groups as F-calculated (0.14) is less than F-critical (0.19) and t-statistic (0.27) is less than t-critical (2.44). The results of the analysis of differences indicated that there were no statistically significant differences in the mean of $\%NH_3$ obtained scores for both potentiometric and visual indicator titration. In other words, both titration methods yielded similar and comparable results.

Potentiometric titration vs visual indicator (hydrochloric acid)

The experiment was further investigated with the purpose to evaluate the performance of two titration methods (potentiometric and visual indicator titration) using HCl. Figure 3 illustrates the overall performance of both titration methods. As shown in Table 5, the average %NH_3 by potentiometric titration ranged from 0.59 to 0.62 while the mean values for visual indicator titration ranged from 0.60 to 0.62. However, in general, it was observed that both titration methods yielded similar mean values (0.61%) with the difference of 0.26% between CV for both titration methods. The data was further analysed by statistical analysis using F-test and t-test, from which the results obtained were tabulated as in Table 6.

Table 5. Comparison results between potentiometric titration vs visual indicator

Titration Method (HCl)	Mean of NH_3 (%)	
	Potentiometric	Visual
HA-1	0.59	0.61
HA-2	0.61	0.62
HA-3	0.61	0.60
HA-4	0.60	0.60
HA-5	0.60	0.62
HA-6	0.62	0.61
average	0.61	0.61
sd	0.0105	0.0089
%CV	1.73	1.47
min	0.59	0.60
max	0.62	0.62

Figure 3. Potentiometric titration vs visual indicator (hydrochloric acid)

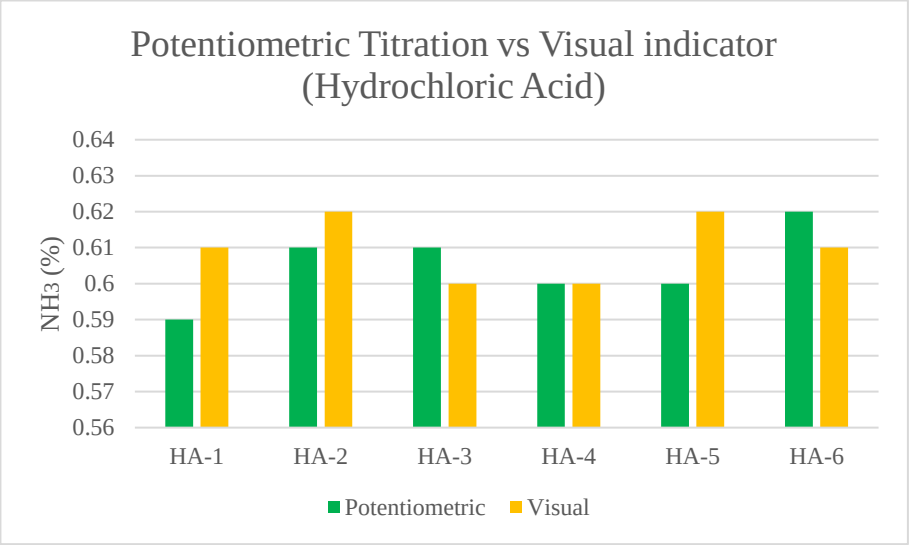

Table 6. Summary of F-test and t-test

Statistical Parameter	Value
F calculated	1.38
F critical	5.05
P value	0.39
t statistic/calculated	0.27
t critical	2.22

As shown in Table 6, statistical analysis of F-test and t-test were conducted to reveal if there were significant differences in the mean of NH_3 by both potentiometric and visual indicator titration. The interaction between measurement was indicated by p-value (0.39) which yielded more than $\alpha = 0.05$, thus the data was further analysed by using t-test to assess and evaluate the significant difference of the mean value between potentiometric and visual indicator titration. The analysed data showed there was no statistically significant difference between the two groups as the F-calculated (1.38) is less than F-critical (5.05), whereas t-statistic (0.27) is less than t-critical (2.22). The results of the analysis of differences indicated that there were no statistically significant differences in the mean of $\%NH_3$ obtained scores for both potentiometric and visual indicator titration. In summary, both titration methods produce comparable results.

Interlaboratory Testing Programme

As mentioned by Nur Salwanie *et al.*, 2011, the application of Interlaboratory Testing Programme (ITP) has been extensively used at both national and international levels. This programme served several purposes such as the evaluation of participants performances against pre-established criteria by means of interlaboratory comparisons and assessment of precision of testing procedures in terms of its repeatability *(r)* and reproducibility *(R)*. Participants are given the sufficiently homogeneous materials and follow the same requirements and procedures in performing the tests. This will help to generate the precision statement based on values of *r* and *R* as part of ISO/IEC 17025 accreditation requirements under quality assurance and calibration. In other words, proficiency testing (PT) is a method used to demonstrate competency and validate a laboratory's measurement process by comparing the laboratory's own results to the results of a reference laboratory and other participant laboratories (ISO/IEC 17043, 2010 and ISO/IEC 17025, 2017).

Apart from that, proficiency testing provides a platform for the laboratory to demonstrate competency for a particular measurement discipline which can be used to validate measurement methods, technical training of personnels, traceability of standards and estimation of measurement uncertainty (ISO/IEC 17043, 2010). As specified in ISO/IEC 17025, 2017, the information on proficiency testing is proven useful for those laboratories seeking accreditation of ISO/IEC 17025:2017 to demonstrate the technical competency of their calibration and testing laboratories as per requirement in the scheme.

The special ITP was conducted in October 2018 to gauge the competency of each participating laboratory in conducting the test procedure for the determination of alkalinity (NH_3) content by both acids and both titration methods. A total of 13 independent laboratories involved in this programme and 50 kg of low ammoniated latex concentrate (LA-latex) obtained from MARDEC Industrial Latex Sdn. Bhd. in Tapah, Perak was used in this ITP. The homogenisation of LA-latex concentrate was conducted by the MRB Proficiency Testing Provider (MRB-PTP) following a standard protocol in the ISO Guide 35, 2017, prior to distribution of proficiency testing (PT) samples to the respective participating laboratories.

The homogeneity study is one of the important elements in proficiency testing. According to ISO Guide 35, 2017, homogeneity is defined as the quality or state of being of a similar kind or of having a uniformed structure or composition throughout *i.e.*, the quality or state of being homogeneous. A total of ten (10) selected samples bottle was randomly chosen based on stratified random sampling (Table 7) and these samples were tested for homogeneity testing. Outlier tests such as Dixon, Grubb and Cochrane tests were performed to evaluate the data for homogeneity (Dewi *et al.*, 2016). The results were evaluated using various statistical analyses such as F-test, t-test, and analysis of ANOVA on linear regression (Irwin and Marylees, 2013) which demonstrated no significant difference for between bottle results, thus indicated that the PT samples (LA-latex) are sufficiently homogenous. After PT samples were deemed sufficiently homogenised, the PT samples were successfully distributed to respective participating laboratories that had been provided with designated code for reference purposes (Table 8).

Table 7. Stratified random sampling (LA-latex)

Stratum no	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Bottle number (LA-LATEX)	1	14	27	40	53	66	79	92	105	118
	2	15	28	41	54	67	80	93	106	119
	3	16	29	42	55	68	81	94	107	120
	4	17	30	43	56	69	82	95	108	121
	5	18	31	44	57	70	83	96	109	122
	6	19	32	45	58	71	84	97	110	123
	7	20	33	46	59	72	85	98	111	124
	8	21	34	47	60	73	86	99	112	125
	9	22	35	48	61	74	87	100	113	126
	10	23	36	49	62	75	88	101	114	127
	11	24	37	50	63	76	89	102	115	128
	12	25	38	51	64	77	90	103	116	129
	13	26	39	52	65	78	91	104	117	130

Random bottle number chosen	10	26	36	45	55	74	83	102	117	120

Table 8. List of participants in Interlaboratory Proficiency Testing

Lab Code	Laboratory
A1	Regulatory and Quality Assurance Unit (RQAP), 260 Jalan Ampang
A2	Global Testing and Consultancy for Rubber (G-TAC$_R$), 260 Jalan Ampang
A3	Rubber Research Institute of Vietnam (RRIV)
A4	Malayan Testing Laboratory Sdn Bhd (Kedah)
A5	Technology & Quality Control Centre (TQCC)
A6	Global Testing and Consultancy for Rubber (G-TAC$_R$), Sg. Petani
A7	Revertex
A8	Synthomer (M)- Incoming- NR Lab
A9	Weir Mineral Malaysia
A10	Sime Darby Research Sdn. Bhd.
A11	Bard Sdn. Bhd
A12	MARDEC Industrial Latex Sdn. Bhd. (Tapah)
A13	MARDEC Industrial Latex Sdn. Bhd. (Ulu Ara)

All calculations to provide repeatability and reproducibility values were performed in accordance to ISO 19983, 2017. A “type-1” precision was evaluated based on the method of preparation of the latex samples used for the ITP. The precision value expressed as 95% confidence level from the ITP was provided in terms of *r* and *R* by which outliers generated from repeatability and reproducibility will be flagged by “K” and “H” respectively (ISO 19983:2017). The closer *r* and *R* values to zero indicates better repeatability and reproducibility, respectively.

The software commercially known as the MRB e-Precision system (Nur Salwanie *et al.*, 2011) is used to perform the calculations and producing tables and graphs associated with the standard practice of conducting an interlaboratory study to determine the precision of a test method ((ISO 19983:2017 and ISO 13528, 2015). The software is a web-based system produced in-house by the MRB to analyse data obtained from the proficiency testing. This versatile, robust and user-friendly system is not only able to provide the precision values obtained from the PT programme in terms of *r* and *R*, it is also capable of treating outliers data which is a plus point as other commercially available software fails to offer (Nur Salwanie and Faridah Hanim, 2017). The treated values are used to establish a precision statement which is an essential element in any national and/or international standards.

The overall performance of participants either using both sulfuric acid and hydrochloric acid as well as both titration methods of potentiometric and visual indicator were tabulated and summarised in Tables 9 to 12. From the findings, all laboratories that took part in the ITP were neither “H” nor “K” flagged for both types of acids and titration methods, which indicate that 100% of the total participants performed well in the ITP.

Table 9. Summary of Interlaboratory Proficiency Testing (potentiometric titration with sulfuric acid)

Lab Code	r_1	r_2	r_3	r_4	x'	s	d	h	k	Flagged "H"	Flagged "K"
A1	0.20	0.20	0.20	0.21	0.20	0.005	-0.005	-0.577	1.00	-	-
A2	0.21	0.20	0.20	0.20	0.20	0.005	-0.005	-0.577	1.00	-	-
A3	0.22	0.23	0.22	0.22	0.22	0.005	0.005	1.732	1.00	-	-
A4	0.20	0.20	0.19	0.19	0.20	0.006	-0.003	-1.443	1.15	-	-
A5	0.22	0.21	0.21	0.20	0.21	0.008	0.003	0.289	1.63	-	-
A6	0.21	0.21	0.21	0.21	0.21	0.000	0.003	0.289	0.00	-	-
A11	0.21	0.21	0.21	0.21	0.21	0.000	0.003	0.289	0.00	-	-

cell = test result of a laboratory	Average of cell averages, x" =	0.208
x' = cell average	Standard deviation of cell averages, sx' =	0.009
s = cell standard deviation	Repeatability standard deviation, sr =	0.005
d = cell deviation = x' - x"	Reproducibility standard deviation, sR =	0.010
h = d/s(x')	Repeatability, r =	0.014
k = s/sr	Reproducibility, R =	0.027
r_1, r_2 = Day1 (measurement)		
r_3, r_4 = Day2 (measurement)		

Table 10. Summary of Interlaboratory Proficiency Testing (visual indicator titration with sulfuric acid)

Lab Code	r_1	r_2	r_3	r_4	x'	s	d	h	k	Flagged "H"	Flagged "K"
A1	0.21	0.22	0.22	0.22	0.22	0.005	0.001	0.089	0.09	-	-
A2	0.22	0.22	0.21	0.21	0.22	0.006	-0.001	-0.071	1.06	-	-
A3	0.24	0.23	0.23	0.23	0.23	0.005	0.016	1.046	0.92	-	-
A4	0.20	0.20	0.20	0.20	0.20	0.000	-0.016	-1.028	0.00	-	-
A6	0.26	0.25	0.24	0.24	0.25	0.010	0.031	2.003	1.76	-	-
A8	0.26	0.25	0.24	0.24	0.25	0.010	-0.011	-0.709	1.06	-	-
A9	0.20	0.21	0.20	0.20	0.20	0.005	-0.014	-0.869	0.92	-	-
A10	0.22	0.22	0.22	0.22	0.22	0.000	0.004	0.248	0.00	-	-
A11	0.20	0.21	0.21	0.20	0.21	0.006	-0.011	-0.709	1.06	-	-

cell = test result of a laboratory	Average of cell averages, x" =	0.216
x' = cell average	Standard deviation of cell averages, sx' =	0.016
s = cell standard deviation	Repeatability standard deviation, sr =	0.005
d = cell deviation = x' - x"	Reproducibility standard deviation, sR =	0.016
h = d/s(x')	Repeatability, r =	0.015
k = s/sr	Reproducibility, R =	0.046
r_1, r_2 = Day1 (measurement)		
r_3, r_4 = Day2 (measurement)		

Table 11. Summary of Interlaboratory Proficiency Testing (potentiometric titration with hydrocloric acid)

Lab Code	r_1	r_2	r_3	r_4	x'	s	d	h	k	Flagged "H"	Flagged "K"
A1	0.16	0.16	0.17	0.17	0.17	0.006	0.001	0.089	0.09	-	-
A2	0.17	0.17	0.17	0.17	0.17	0.000	-0.001	-0.071	1.06	-	-
A3	0.20	0.20	0.21	0.21	0.21	0.004	0.016	1.046	0.92	-	-
A4	0.22	0.22	0.19	0.19	0.21	0.017	-0.016	-1.028	0.00	-	-
A6	0.21	0.21	0.21	0.21	0.21	0.000	0.031	2.003	1.76	-	-
A7	0.18	0.18	0.20	0.20	0.19	0.012	-0.011	-0.709	1.06	-	-
A11	0.22	0.21	0.21	0.21	0.21	0.004	-0.014	-0.869	0.92	-	-
A12	0.22	0.22	0.22	0.22	0.22	0.000	0.004	0.248	0.00	-	-
A13	0.22	0.22	0.21	0.21	0.22	0.006	-0.011	-0.709	1.06	-	-

cell = test result of a laboratory	Average of cell averages, x" =	0.199
x' = cell average	Standard deviation of cell averages, sx' =	0.020
s = cell standard deviation	Repeatability standard deviation, sr =	0.005
d = cell deviation = x' - x"	Reproducibility standard deviation, sR =	0.020
h = d/s(x')	Repeatability, r =	0.015
k = s/sr	Reproducibility, R =	0.058
r_1, r_2 = Day1 (measurement)		
r_3, r_4 = Day2 (measurement)		

Table 12. Summary of Interlaboratory Testing Programme (visual indicator titration with hydrochloric acid)

Lab Code	r_1	r_2	r_3	r_4	x'	s	d	h	k	Flagged "H"	Flagged "K"
A1	0.17	0.18	0.18	0.18	0.18	0.005	0.001	0.089	0.09	-	-
A2	0.17	0.18	0.18	0.18	0.18	0.005	-0.001	-0.071	1.06	-	-
A3	0.21	0.21	0.21	0.22	0.21	0.005	0.016	1.046	0.92	-	-
A4	0.21	0.20	0.20	0.20	0.20	0.005	-0.016	-1.028	0.00	-	-
A6	0.24	0.23	0.22	0.22	0.23	0.010	0.031	2.003	1.76	-	-
A7	0.20	0.19	0.21	0.21	0.20	0.010	-0.011	-0.709	1.06	-	-
A11	0.20	0.20	0.21	0.21	0.21	0.003	-0.014	-0.869	0.92	-	-
A12	0.22	0.22	0.22	0.22	0.22	0.000	0.004	0.248	0.00	-	-

cell = test result of a laboratory	Average of cell averages, x" =	0.2028
x' = cell average	Standard deviation of cell averages, sx' =	0.0179
s = cell standard deviation	Repeatability standard deviation, sr =	0.0067
d = cell deviation = x' - x"	Reproducibility standard deviation, sR =	0.0188
h = d/s(x')	Repeatability, r =	0.0191
k = s/sr	Reproducibility, R =	0.0533
r_1, r_2 = Day1 (measurement)		
r_3, r_4 = Day2 (measurement)		

In addition, the overall mean of NH_3 and standard deviation (SD) for potentiometric and visual indicator titration and H_2SO_4 and HCl; were calculated and plotted in a quality control (QC) chart to monitor the overall performance of each participating individual laboratory in the ITP. The upper control limit and lower control limit were constructed using the formula: [Mean ± (2 x SD)], while the performances of individual laboratory participants are considered as good and satisfactory if they recorded the NH_3 values which lies within the acceptable ranged of control limits for each measurement.

The overall performance of all participants is illustrated in Figures 4 to 7, respectively. In general, the QC charts obtained indicate that all laboratories produce excellent performances and results from this ITP, which is essential for the respective laboratories in monitoring their own performances against other laboratories.

Other than that, the main purpose of this ITP which is to gauge the competency of each participating laboratory in conducting the standard test procedure (ISO 125, 2020) was successfully achieved. The overall performance in terms of *r* and *R* among participating laboratories in conducting the test procedure for the determination of alkalinity (NH_3) content by both acids and both titration methods were excellent.

Figure 4. Performance of participants in Interlaboratory Testing Programme
(Potentiometric titration with sulfuric acid)

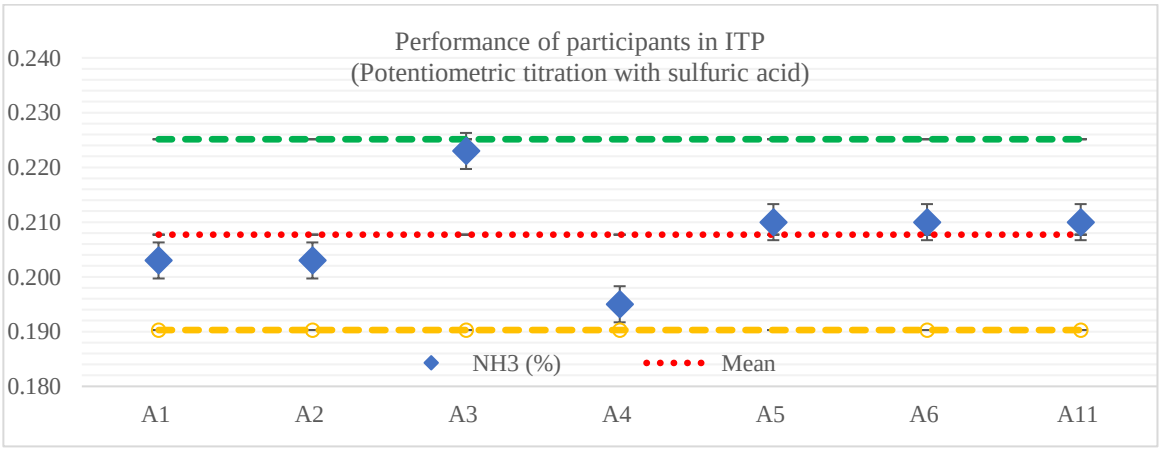

Figure 5. Performance of participants in Interlaboratory Testing Programme
(Visual indicator titration with sulfuric acid)

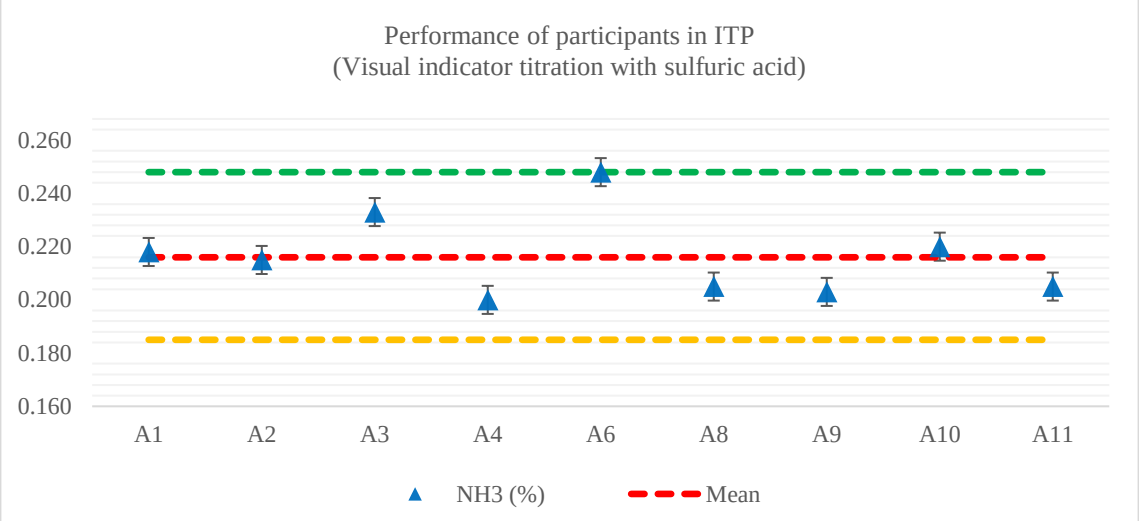

Figure 6. Performance of participants in Interlaboratory Testing Programme
(Potentiometric titration with hydrochloric acid)

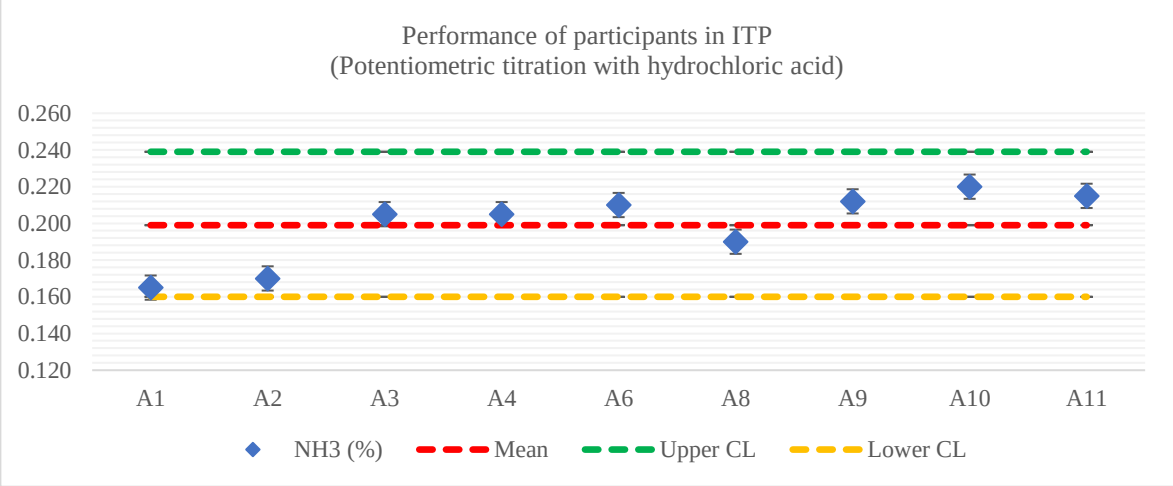

Figure 7. Performance of participants in Interlaboratory Testing Programme
(Visual indicator titration with hydrocloric acid)

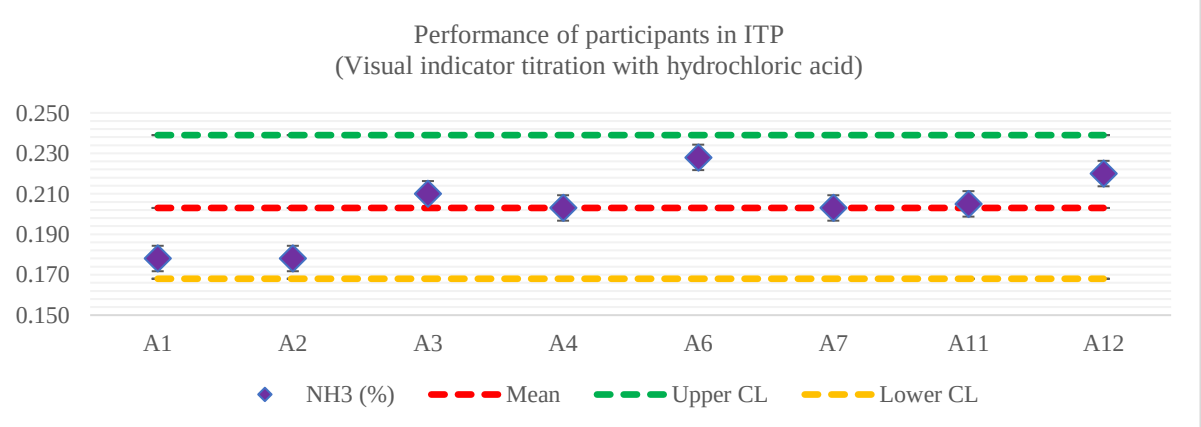

Table 13 summarises the new precision statement for the test method which was established in terms of *r* and *R*. The overall mean of $\%NH_3$ for all methods of determination ranging from 0.20 to 0.22. The *r* of measurement for all methods ranged from 0.01 to 0.02 while for *R*, it lies within 0.03 to 0.06. The potentiometric titration with H_2SO_4 produced the smallest s_r (0.005) which is within the laboratory standard deviation, while for the determination using visual indicator titration with HCl produced the highest s_r (0.007). On the other hand, the procedure using potentiometric titration with HCl gave the biggest value of S_R, (0.020) between the laboratory standard deviation, followed by visual indicator titration with HCl (S_R = 0.019). It was observed that potentiometric titration with H_2SO_4 produced the lowest S_R values (0.010) followed by visual indicator titration with H_2SO_4 (S_R values = 0.016). In summary, the establishment of new precision data is well accepted consensusly by the technical committee of ISO/TC45/SC3/WG2 (expert group) and has been incorporated in the latest version of ISO 125:2020. The precision data obtained is more comprehensive, details and dedicated compared to the previous version of ISO 125:2011.

Table 13. Summary of precision data

Method of determination	Average results	Within-laboratory		Between laboratories	
		s_r	r	s_R	R
Potentiometric titration with H_2SO_4	0.21	0.005	0.01	0.010	0.03
Visual indicator titration with H_2SO_4	0.22	0.005	0.02	0.016	0.05
Potentiometric titration with HCl	0.20	0.005	0.02	0.020	0.06
Visual indicator titration with HCl	0.20	0.007	0.02	0.019	0.05

r is the repeatability (in measurement units);
s_r is the within-laboratory standard deviation;
R is the reproducibility (in measurement units);
s_R is the between-laboratory standard deviation.

CONCLUSION

The finding from this study is important to support the revision work of the ISO 125 at the international level. As alkalinity is one of the essential parameters for specification of latex concentrate, this paper successfully demonstrated that the standard test method of ISO 125 has been properly revised. With the establishment of proper procedure for standardisation of sulfuric acid and hydrochloric acid in this revision work, it is very beneficial to the accredited testing laboratories and rubber producers as this newly revised test method is going to be used for standard compliance in latex specification, thus ensuring that the tests are reliable and accurate.

The most important contribution of this paper is the establishment of new precision data for the test method, generated from the ITP. The new precision data was successfully incorporated in the latest version of ISO 125:2020. This is very essential and significant improvement as the precision data obtained is more comprehensive compared to the previous version of ISO 125:2011. The new edition (seventh edition) of ISO 125:2020 was published in February 2020, and this seventh edition replaces the sixth edition (ISO 125:2011).

The technical data comprises of comparative studies between both acids and both titration techniques for determination of alkalinity content in NR latex concentrate has been successfully established. The findings have given an alternative to those laboratories to perform which titration method that they preferred, either by potentiometric titration or visual indicator titration as both titration methods yielded comparable results. Other than that, this paper has demonstrated that both sulfuric and hydrochloric acids can be used to obtain similar and comparable results.

This paper highlighted the significant contribution of the MRB in standards development (standardisation) which is able to safeguard the interest and sustainability of the Malaysian rubber industry. Another impact of this revision work is, it enables the establishment of standard test methods in compliance to the international legislations, thus enhances the image and credibility of the MRB, especially at the international levels as an expert body in the development of standard test methods for NR latex.

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