Improving precision in rubber test methods

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Introduction

It is about 25 years since ISO TC 45 Rubber and Rubber products started to perform ITP´s (Inter laboratory Test Programs), to investigate the precision of test methods. The results from the ITP´s are then included in the relevant standard as a precision clause giving information about the repeatability (within lab) and reproducibility (between labs) of the test method.

The precision data can be used as part of the input to estimate the uncertainty of a test result, which is required by accredited laboratories.

Many test methods showed however very disappointing and poor precision results, see table 1. To investigate the reasons for the poor precision a project was started in Sweden in the end of the eighties (1,2,3). This project investigated the factors contributing to variation in test results for hardness tests, tensile tests, heat ageing tests and TR-tests. Suggestions were made for improvements in the test methods and in the instruments and many of these have now been adopted in ISO standards and in modern instruments.

Many of the ITP´s were done several years ago with analogue instruments sensitive to operator influence. During the last 10 years digital, automated and computerised instruments have been introduced on the market and the precision clauses in the standards may not be representative of modern best practice.

This paper includes the results from investigations, during the last 25 years , of some rubber test methods to identify the factors giving poor precision and results made with modern instruments will be compared with the tests made with older instruments.

Table 1

Present reproducibilities

ISO-no.	Test method	Uncertainty *
ISO 34-1	Tear Test, method A	± 36 %
ISO 34-1	Tear Test, method B	± 37 %
ISO 34-1	Tear Test, method C	± 30 %
ISO 37	Tensile Test	No ITP published
ISO 48	Hardness, metod N	± 1,75 IRHD
ISO 48	Hardness, method M	± 3,2 IRHD
ISO 188	Ageing, method A, change in hardness	± 38 %
ISO 188	Ageing, method A, change in Eb	± 25 %
ISO 815	Compression set at 100 °C	± 18 %
ISO 815	Compression set at –25 °C	± 75 %
ISO 1817	Effect of liquids	No ITP done
ISO 2921	TR-test	No ITP done
ISO 3384	Stress Relaxation method A, 100 °C	± 6 %
ISO 3384	Stress Relaxation method B, 100 °C	± 18 %
ISO 6914	Stress Relaxation in tension, method A	No ITP done
ISO 7619	Hardness	± 2,5 Shore A

*The given uncertainty is half the reproducibility assuming a symmetric distribution.

Definitions

Distinction is made between two types of variability – repeatability and reproducibility.

Repeatability is the variability within any given lab which will depend on the quality of testing in that lab. It is useful for comparison of test results within that lab for purposes of technical development, etc.

Reproducibility is the variability between laboratories – hope-fully those with good quality of testing. It is useful in producer-consumer acceptance and other inter-lab comparisons.

Swedish Project

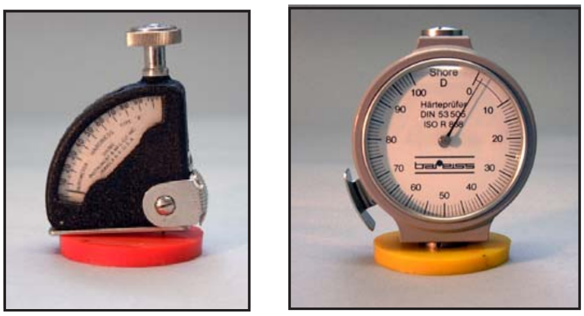
A project with 12 laboratories started 1989 to study the factors influencing the test results, with the aim of improving the precision. The following test methods were investigated.

- Hardness Shore A
- IRHD N
- IRHD M
- Tensile tests
- Heat ageing tests
- TR tests

Hardness (1)

For hardness tests the following factors were investigated by one operator visiting all laboratories and bringing with him test samples and hardness testers. The tests were then made with his testers and with the hardness testers of each laboratory.

- Equipment
- Operator
- Temperature
- Thickness
- Applied load (Shore)



Picture 1

Picture 2

Picture 1 shows old types of Shore Durometers and **picture 2** shows old types of IRHD testers.

Operator and equipment influence

In the table 2 below we can see the results from an ITP made 1987

Table 2

	Mean	R	(R)
IRHD-N	60,5	4,1	6,8
IRHD-M	60,8	5,5	9,0
Shore A	60,9	7,3	12,0

R = actual units (R) = %

In table 3 we can see the results regarding the operator and equipments influences for IRHD-N:

Table 3

IRHD N	Mean	R	(R)
Different operators and different testers	59,8	3,0	5,1
Different operators and the same tester	59,8	3,0	5,1
One operator and different testers	59,4	1,4	2,4
One operator and the same tester	59,4	1,8	3,1

R = actual units (R) = %

In table 4 we can see the results for IRHD-M:

Table 4

IRHD M	Mean	R	(R)
Different operators and different testers	62,2	3,2	5,2
One operator and different testers	62,0	2,8	4,5

R = actual units (R) = %

In table 5 we can see the results for Shore A:

Table 5

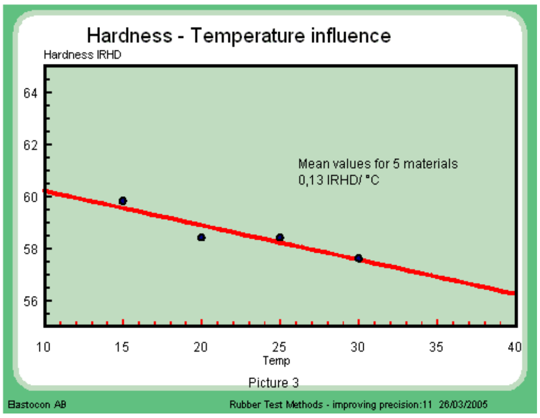
Shore A	Mean	R	(R)
Different operators and different testers	61,0	4,6	7,5
Different operators and the same tester	59,7	3,2	5,3
One operator and different testers	61,2	3,1	5,1
One operator and the same tester	61,3	1,8	3,0

R = actual units (R) = %

Temperature influence

In picture 3 we can see the influence of temperature. 5 materials were tested between 15 to 30 °C and the hardness were measured.

The result shows that if a laboratory with a constant room with a temperature control of the normally specified ± 2 °C makes tests within this range, the variation correspond to 0,5 hardness degrees.



Picture 3

Thickness influence

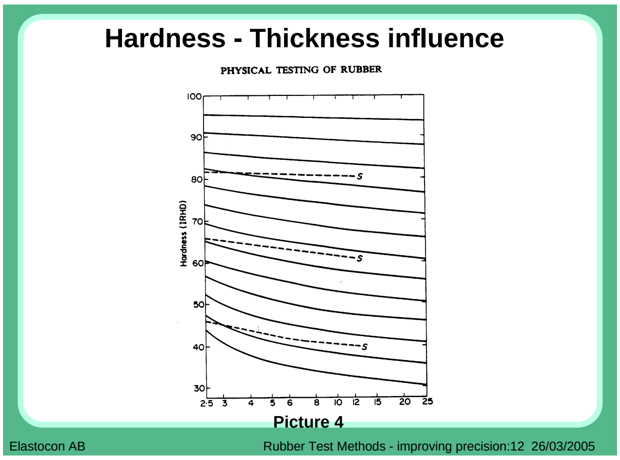
The influence of thickness was found in the literature. In Physical testing of Rubber by Roger Brown picture 4 was found, which shows that IRHD is more sensitive for the thickness than Shore A and that the error is higher for soft materials.

Influence of applied load (Shore A)

For Shore measurements the applied load on the foot is important for the result and it may be a good practise to let the operators of hand held Shore Durometers to practise measurements on a balance. Table 6 shows the error to be in the range of 2,5 Sh A when using the correct 1 kg compared to using 5 kg. The error is greater on softer samples.

Table 6

Shore A	Load	Mean	Increase
First series, 11 samples	1 kg	60,6	
	5 kg	63,1	2,5
Second series, 7 samples	1 kg	60,6	
	5 kg	62,8	2,2



Hardness - Thickness influence

PHYSICAL TESTING OF RUBBER

Picture 4

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Picture 4

Summary of influences for hardness

Table 7 summaries the influences of the different factors.

Table 7

Method	R	
IRHD-N		
Equipment	0,4	
Operator	1,6	
Temperature	0,13	per °C
Thickness	2,0	from 4 to 10 mm
IRHD-M		
Equipment	2,8	
Operator	0,3	
Shore A		
Equipment	1,4	
Operator	1,5	
Load	2,4	from 1 to 5 kg
Thickness	1,5	from 4 - 10 mm

Recommended actions

In the report published 1993 (1) the following actions were recommended. Now many years later we can see that most of them are now reality in new instruments and revised test standards, see table 8.

Table 8

IRHD-N

- Eliminate the friction inside the dial gauge
- Automatic timing of zero time and measuring time
- Automatic lowering of zero load and measuring load

IRHD-M

- The same as for IRHD-N

Shore A

- Use of a constant load
- Increasing the measuring time to 3 s
- Regular calibration and adjustment

Table 9 shows a recent ITP for hardness done in March 2005 with digital modern hardness testers. The results shows improvement over the 1987 ITP, especially for the Shore A and IRHD-M scales.

Table 9

	Mean	**r**	**(r)**	**R**	**(R)**
IRHD-N	63,6	1,8	2,8	3,4	5,3
IRHD-M	63,9	1,2	2,1	3,6	6,2
Shore A	62,3	1,4	2,4	3,8	5,9

R = actual units

(R) = %

Picture 5 shows new types of hardness testers with timer and constant load.

Picture 5

All scales All scales Shore scales

Tensile Tests

In table 10 we can see the factors studied for tensile tests:

Table 10

- Calibration
- Equipment
- Test conditions
- Test piece preparation
- Thickness measurement

Table 11 shows the results from an ITP in 1987.

Table 11

	Mean	**R**	**(R)**
Tensile strength, MPa	13,9	2,1	15,1
Elongation at break, %	504	85	17,0
Stress at 100 %	2,5	0,48	19,4

R = actual units (R) = %

Influence of calibration

Table 12 shows the variation in force value when a weight of 5 kg was attached to the different tensile testers:

Table 12

Mean	**R**	**(R)**
49,20	1,46	2,97

Number of test pieces

Table 13 shows the improvement in tensile strength and elongation at break, when using 5 test pieces instead of three.

Table 13

Three test pieces	**Mean**	**R**	**(R)**
Tensile strength, MPa	16,6	1,75	10,6
Elongation at break, %	459	88	19,1
Stress at 100 %	2,4	0,37	15,3
Five test pieces	**Mean**	**R**	**(R)**
Tensile strength, MPa	16,5	1,44	8,7
Elongation at break, %	459	82	17,9
Stress at 100 %	2,4	0,37	15,3

R = actual units (R) = %

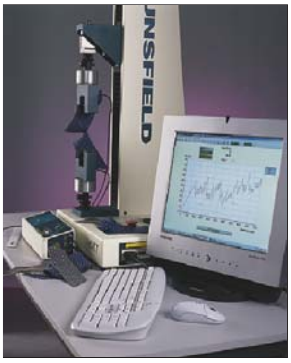
Summary of influences for tensile tests

Table 14 shows a summary of the factors influencing tensile tests.

Table 14

Factor	**(R)**
Calibration	1,8
Thickness measurement	1,2
Cutting of test pieces	1,3
Using 5 instead of 3 test pieces	1,9

Picture 6 shows a modern single column tensile tester and a dual column tensile tester, with an accuracy of 0,5 % of the force reading.

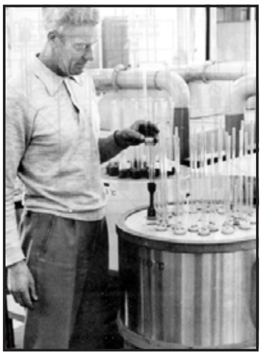


Ageing Tests (3)

In table 15 are the factors which were investigated for ageing tests listed:

Table 15

- temperature uniformity in time
- temperature uniformity in space
- air speeds
- air exchange rates
- ageing results in different ovens



Picture 7 shows an old cell oven which shows that the factors of constant temperature, air exchange rate and separating the materials under test, were already observed when ISO 188 was written.

Picture 8 shows heating ovens with fans used for ageing. The fans give a uniform temperature, but high and uneven air speed.

Ageing test reproducibility

Table 16 shows the results from an ITP with 12 laboratories in 1988.

Table 16

Property	Mean	R	(R)
Change in Ts, %	-18	15	83
Change in Eb, % -	40	16	40
Change in IRHD-M	-13	10	77

R= in actual units (R)= in %

Temperature influence

Temperature tolerances in ISO 23529 are ± 1 °C up to and including 100 °C, ± 2 °C, 100 °C and up ± 2 h time tolerance at test times 1 week or longer. 1 °C wrong temperature corresponds to 10 % in testing time at an Arrheniusfactor of 2, and 15 % at a factor of 2,5.

This means that two laboratories can be 60 % from each other at a test at 125 °C and they are still within the specification.

The following ovens were investigated more in detail.

Table 17

- Heraeaus UT 5042
- Heraueus UT 5060 E
- Salvis TSW 60
- Elastocon EB 01
- Elastocon EB 04

In table 18 we can see that a modern electronic controller can keep a constant temperature, the oven 5042 had a mechanical controller and is not suitable for ageing.

Table 18

Oven	5042	5060E	TSW 60	EB 01	EB 04
°C	13,8	0,1	0,2	0,1	0,1

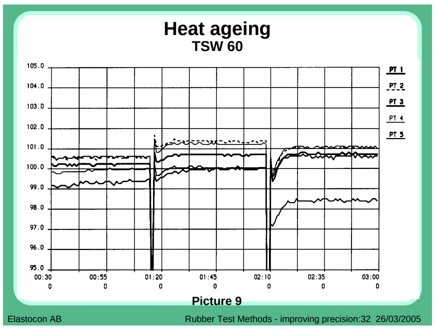
Table 19 shows the variation in space in 15 locations in the ovens 50 mm from the walls and in the centre. The temperature was measured in 5 locations at a time as the sensors were mounted in a frame with five sensors and moved between three positions in the ovens.

Table 19

Location	5042	5060E	TSW 60	EB 01	EB 04	
Inner	0,9	0,5	1,3	NA	0,4	
Centre	0,7	1,7	1,3	NA	0,3	
Outer	0,7	1,1	2,7	NA	0,2	
Total	1,2	1,7	3,1	0,5	0,4	Values in °C

Picture 9 and 10 shows graphically the difference between the TSW 60 oven and the EB 04 oven. The drops are when the frame with the sensors is moved and the door is opened.

Picture 11 shows the elongation at break from two compounds tested at three temperatures with 5 °C interval. The result is quite dependant of the ageing temperature, especially for the NR where the 100 °C seems to be a too high temperature.



Heat ageing

TSW 60

Picture 9

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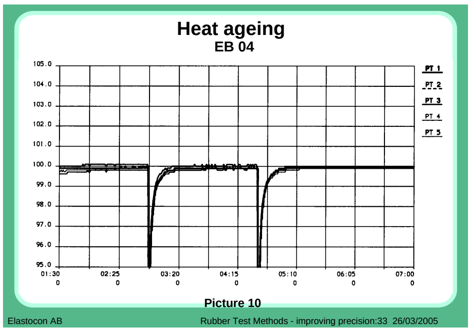

Heat ageing

EB 04

Picture 10

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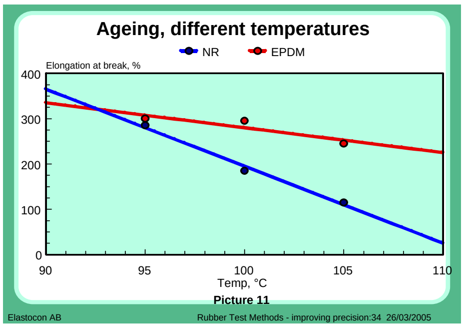

Ageing, different temperatures

Picture 11

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Picture 9

Picture 10

Picture 11

Influence of the air exchange rate

Table 20 shows the measured air exchange rates in the tested ovens. The influence of air exchange rates has been investigated in an ISO ITP and the results showed no real difference in ageing properties between 3 or 10 changes per hour. At zero changes however drastic differences was found.

It seems as the tolerances in ISO 188 is satisfactory with 3 to 10 changes per hour to keep the oxygen concentration constant and ventilate away degradation products.

Table 20

Oven	5042	5060E	TSW 60	EB 01 *	EB 04*	
Open exhaust	~160	~40	~300	20	16	
Closed exhaust	0	0	20	0	0	air changes per hour

* can be set at specified value by a needle valve and a flowmeter

Air speed influence

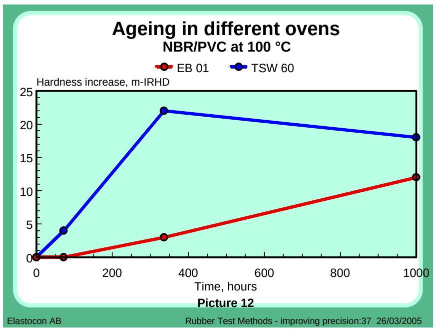
Table 21 shows the air speed measured in the ovens.
In EB 01 and EB 04 is the air speed dependant of the air exchange rate only.

Table 21

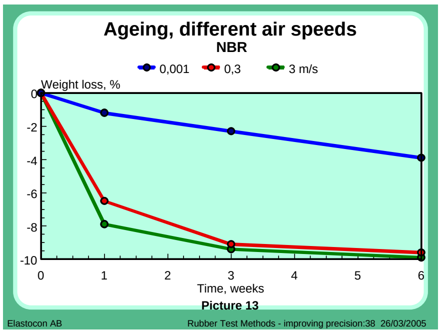
Speed	5042	5060E	TSW 60	EB 01	EB 04	
Min speed	0,5	0,0	0,4	<0,001	<0,001	
Max speed	2,6	4,5	3,0	<0,001	<0,001	Speed in m/s

Picture 12 shows ageing of an NBR/PVC compound in two ovens were the only difference is the air speed. The automotive specification allowed a maximum of 15 IRHD-M hardness increase during 1 000 h of ageing. In the traditional oven with high air speed the hardness increase was 17 IRHD-M and in the oven with low air speed it was 13 IRHD-M, but the road to the end values were quite different.

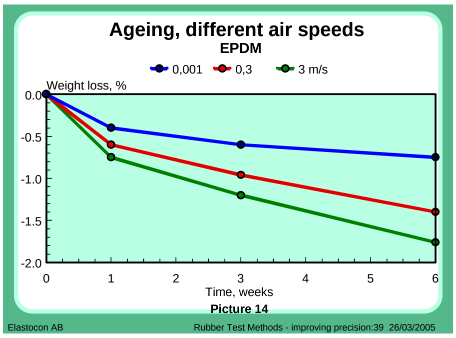
In picture 13 and 14 the results from NBR and EPDM compounds being tested at different air speeds is shown. The weight loss during a 1 000 h ageing test shows very clearly the effect of the air speed. The evaporation of softeners and antioxidants and the oxidation of the surface are both depending of the air speed .



Picture 12



Picture 13



Picture 14

ISO ITP

The requirement of low air speed, dependant of the air exchange rate only, is now included in ISO 188 method A. A method B with high air speed, 1 m/s of laminar flow, was also introduced in ISO 188.

In table 22 we can see an ITP performed within ISO 1997 and the results are still not very promising, possibly because the participating laboratories are using all different kinds of ovens. ISO 188 is now being revised again and the importance of the temperature will be pointed out and the measurement of the temperature close to the samples with a separate sensor will be required.

Table 22 10 laboratories, ISO ITP 1997

	mean	r	(r)	R	(R)
Change in T_s, %	-7	8,5	121	11,7	167
Change in E_b, %	-24	9,2	38	12,2	50
Change in, IRHD-M	-8,3	4,4	53	6,3	76

Temperature retraction test, TR

The factors listed in table 23 were investigated for the TR-test.

Picture 15

Table 23

- Temperature measurements
- Agitation in the bath
- Length measurements

In picture 15 we can see a traditional manual TR-tester.

Table 24 shows the results from two ITP:s in 1985 and 1987. The results are quite disappointing.

Table 24

	1985	**1987**
	R	**R**
TR10	6,2	5,9
TR30	7,2	7,8
TR50	6,3	11,2
TR70	7,1	12,6

R= reproducibility in actual units of measurements, °C

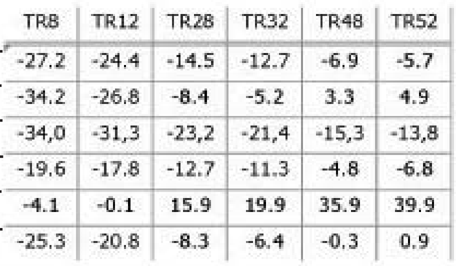
Influence of temperature and agitation

It is important to have a calibrated temperature sensor close to the samples. It is also important with a good agitation, not only in circulation but also from bottom to top of the bath as the cold bath very easily get temperature gradients. This is specially pronounced when CO_2 -ice is used for cooling, as the ice very often accumulates in the bottom of the bath.

Influence of the length measurements.

The present tolerances in ISO 2921 of ± 1 mm gives a tolerance of the 50 mm test piece of ± 2 % or TR 8 -12 for TR 10. This corresponds to a temperature difference of up to 7 °C. This is shown in Table 25.

TR test report

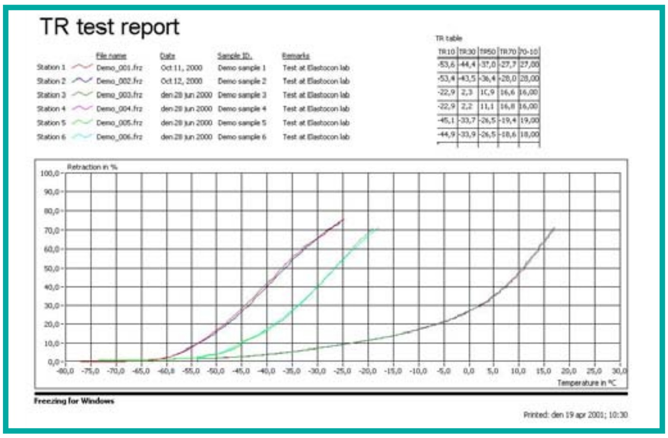


Material	TR8	TR12	TR28	TR32	TR48	TR52
1	-27.2	-24.4	-14.5	-12.7	-6.9	-5.7
2	-34.2	-26.8	-8.4	-5.2	3.3	4.9
3	-34,0	-31,3	-23,2	-21,4	-15,3	-13,8
4	-19.6	-17.8	-12.7	-11.3	-4.8	-6.8
5	-4.1	-0.1	15.9	19.9	35.9	39.9
6	-25.3	-20.8	-8.3	-6.4	-0.3	0.9

Table 25

ISO 2921 is now up for revision and tighter tolerances will be included.

Picture 17 shows the repeatability of a modern computer controlled TR-tester. 2 specimen each of three materials were tested. The instrument is shown in picture 18.


TR test report

	File name	Date	Sample ID.	Remarks
Station 1	Demo_001.frz	Oct 11, 2000	Demo sample 1	Test at Elastocon lab
Station 2	Demo_002.frz	Oct 12, 2000	Demo sample 2	Test at Elastocon lab
Station 3	Demo_003.frz	den 28 jun 2000	Demo sample 3	Test at Elastocon lab
Station 4	Demo_004.frz	den 28 jun 2000	Demo sample 4	Test at Elastocon lab
Station 5	Demo_005.frz	den 28 jun 2000	Demo sample 5	Test at Elastocon lab
Station 6	Demo_006.frz	den 28 jun 2000	Demo sample 6	Test at Elastocon lab

TR table

TR10	TR30	TR50	TR70	70-10
-53,6	-44,4	-37,0	-27,7	27,00
-53,4	-43,5	-36,4	-28,0	28,00
-22,9	2,3	10,9	16,6	16,00
-22,9	2,2	11,1	16,8	16,00
-45,1	-33,7	-26,5	-19,4	19,00
-44,9	-33,9	-26,5	-18,6	18,00

Freezing for Windows

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Picture 17

Picture 18

ISO ITP Project

ISO started to run ITP:s in 1980 but we have not yet been able to prepare precision clauses for all methods.

To improve this situation we have decided in ISO TC 45/SC2 to organize an ITP program which with 4 years interval will perform ITP:s for the most common test methods. This is also of interest for accredited laboratories who needs to participate in ITP:s on a regular basis.

The responsibility to organize the ITP:s will be rotated between the participating laboratories and the test materials will be supplied by specially approved supplier of test materials. It is free of charge to participate, but the test materials may be paid for.

Conclusion

Today when requirements for quality are increasing and tolerances are tightened, we need to be able to measure more accurately. To meet this requirement we need to actively participate in the national and international standardisation work to improve the test methods.

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Key Words: Rubber, Hardness, Tensile, Ageing, Temperature retraction, ITP, Precision.