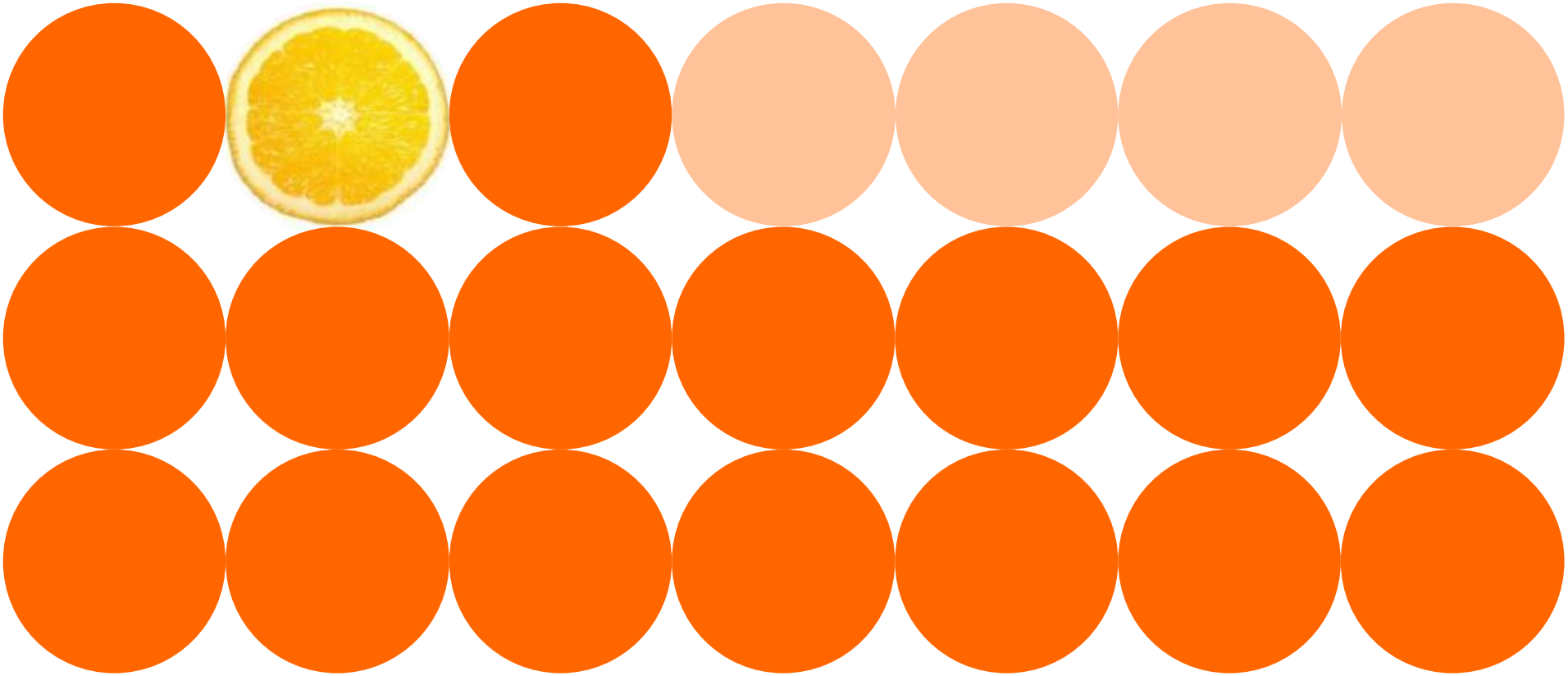
XRF OF AlF_3 – INTERLABORATORY STUDY FOR ISO PRECISION STATEMENT – NOT SO EASY



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AlF_3, ISO, Hydro and Precision

In 2009 Hydro organized and ran an interlaboratory study for x-ray fluorescence elemental analysis of aluminium fluoride.

The purpose was to establish the a precision statement for a new ISO XRF standard.

Eleven laboratories analysed eight materials.

The standard is now voted as a ISO Committee Draft:

ISO CD 12926-1 () — Aluminium fluoride primarily used for the production of aluminium — Determination of elements — Wavelength dispersive X-ray fluorescence spectrometric method — Part 1: Method using pressed powder tablets

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Aluminium fluoride

Aluminium metal is produced by electrolysis, and aluminium fluoride is a key additive to the electrolyte.

Use of AlF_3 is about one Mtonne AlF_3 worldwide, per year.

The production of AlF_3 is done by a number of well established companies, each of which has their own, internal, well established, XRF standard practice. As has the users.

As many as possible should participate in the round robin or interlaboratory study.

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Fluoride Elemental Analysis

Why no AlF3 XRF method before now? WG4 was dormant for 25+ years!

In the list of standards, most are wet chemical, typical examples

- **ISO 4280 (1977) — Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of sulphate content — Barium sulphate gravimetric method**
- **ISO 5930 (1979) — Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of phosphorus content — Reduced molybdophosphate photometric method**
- **ISO 6374 (1981) — Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of phosphorus content — Atomic absorption spectrometric method after extraction**

But industrial practice today is XRF, so the old wet chemical methods are sleeping and a new ISO method is needed.

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Hydro Årdal Participation

The Hydro Årdal application was rewritten for the ISO interlab study, by Katarzyna Mirek-Sliwa.

It was prepared for the ISO ILS, but since early 2009 it has been used hundreds of times for research.

A very good example how the availability of analysis resources generates use.

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ISO

ISO is large, and the formalities from proposal to standard are quite complex. The system ensures all interested parties will be heard, but is slow.

It was a challenge to restart the fluorides work, to make if possible to establish this ISO standard. The 2009 interlab study was the culmination of four years' preparation.

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ISO/TC 226 – The Technical Committee

ISO aims to make up-to-date commercial standards.

Standards for Al electrolysis raw materials are organized around ISO Technical Committee 226, ISO/TC 226:

“Materials for the production of primary aluminium”

- **Primary – made by electrolysis from alumina**
- **Secondary – recycled or otherwise refned**

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ISO/TC 226 – The Standards

ISO/TC 226 manages 100+ standards in several material groups:

- **Electrodes – Carbon Anodes and Cathodes (30+)**
- **Coal Tar Pitch (16)**
- **Petroleum Coke (20)**
- **Alumina (28)**
- **Fluorides (17)**
- **Refractory Fluoride Testing (1)**

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ISO/TC 226 – The Members

P-Member:	O-Member:
AENOR (Spain)	ABNT (Brazil)
ANSI (USA)	AFNOR (France)
BSI (United Kingdom)	ASRO (Romania)
GOST R (Russian Federation)	BDS (Bulgaria)
KATS (Korea, Republic of)	BIS (India)
LNCSM (Libyan Arab Jamahiriya)	DIN (Germany)
NEN (Netherlands)	EOS (Egypt)
SA (Australia)	IRAM (Argentina)
SAC (China)	ISME (Montenegro)
SN (Norway)	ISS (Serbia)
SNV (Switzerland)	ITCHKSAR (Hong Kong, China)
SUTN (Slovakia)	PKN (Poland)
	SFS (Finland)

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ISO/TC 226 – Secretariat

Many countries participate. Norway have long played an important role in standard development in committee ISO/TC 226.

Committee chair is Prof.Em. Dr.Tech. Harald A. Øye

The Secretariat is run by Dr. Elisabeth Hovda of Standard Norge

ISO/TC 226 is supported by both the Norwegian Research Council and the Norwegian Al-industry.

Committee Activities

Systematic reviews of each method, every five years, ending with a vote – with 100+ methods, this means 20+ standards are reviewed each year

Standard writing, requiring 4-5 stages with voting from draft to final published version

The meetings, with votes on work done and new work. Meetings are held every 18 months, the next meeting, the 25th, will be held in Bratislava, April 2011.

Between meetings, a Work Group for each material do the actual development work.

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Restarting WG4 for Fluorides

We had to make sure sufficient countries had an interest and we had to gather Technical Experts.

Standard draft, five countries must approve. Through TC 226 we got involvement from Norway (Hydro, Boliden Odda), USA and China.

Through the Hydro lab network we got involvement from Australia, Slovakia and Slovenia.

More field work generated interest from AlF_3 producers in Italy, Spain, Canada and USA.

The Standard

With sufficient interest gathered, the actual standard development began.

It should have these parts

- **The method writing**
- **The voting and agreement on the draft**
- **The precision statement based on an ILS with the draft method**

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Powder Tablet or Glass Bead?

The plan was two standards, one for glass beads and one for powder tablets.

Good glass beads give better precision due to avoiding grain size influence, but fluorides can volatilize and are aggressive.

Hydro Kurri Kurri and Do-Fluorides used both methods, and for some time Claisse actually had a method published on the internet.

However, with only two labs useing glass beads, an ISO standard was not of interest, and work focused on the pressed powder tablet method.

Questions to Address

Issues

- What elements are important?
- Commercially available calibration sets?
- Sample preparation details, milling, binders, test portion size?
- Channel set-ups in use?

A questionnaire was distributed with good response.

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Example: Calibrations

Company	Country (Laboratory)	Calibration Set
Boliden Odda	Norway	Alcan Set
Derivados del Fluor	Spain	In-house Set
Do-Fluoride Chemicals	China	Do-Fluoride Set
Fluorsid	Italy	In-house Set
Alcoa	USA	In-house Set
Alcoa Mosjøen	Norway	In-house Set
Hydro Kurri Kurri	Australia	Alcan Set
Hydro Ardal PMT	Norway	In-house Set
Rio Tinto Alcan	Canada	Alcan Set
Slovalco	Slovakia	Alcan, In-house
Talum	Slovenia	In-house Set

Calibration Set and Method

The two companies with method and calibration sets, Alcan (now RTA) and Do-Fluorides were contacted, and asked if they would allow us to write the ISO standard around their method.

- **RTA were revising their method and their calibration set.**
- **Do-Fluorides offered to translate their methods to English, both for powder and glass bead specimens.**

So the draft is written based on the Do-Fluorides method together with additional information from Derivados del Fluor, Boliden, Fluorsid, Alcoa, RTA, Slovalco, Talum and the standard practice at Hydro in Norway and Australia.

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Not so Easy

Writing the draft showed the labs used

- **Slightly different sample preparation**
- **Different calibration sets**
- **Different instrumental set-ups**

So how to handle the interlaboratory study? Ideally, the ISO standard should be debated through and agreed on, and then distributed to all to follow closely in the precision statement ILS.

Not so Easy

But the production and use of AlF_3 is done well established companies, each with their own, internal, well established XRF analysis history. Who should change?

This dilemma could not easily be solved, so the solution was to distribute the ILS samples and ask each lab to analyse them with their own method.

Then the standard was written so as to include all sample preparation methods, and all channel set-ups.

Interlaboratory Study – Participants

Boliden Odda AS	Norge	Jorunn Kvåle
Derivados del Flúor S.A.	Espania	Oscar Pérez, Julio de Solaun
Do-Fluorides DFD Chemicals	China	Wu Lin, Xue Xu-jin
Fluorsid S.p.A.	Italia	Luca Pala, Michele Lavanga
Alcoa Point Comfort Laboratory	USA	Suelyn Aschenbeck, Cory Housworth
Alcoa Mosjøen	Norge	John Egil Marken, Tom Andreasen
Hydro Aluminium Kurri Kurri	Australia	Darrell Harman, Grant Foster
Hydro Aluminium Årdal	Norge	Kirsti Gulbrandsen, Kari Holsæter
Rio Tinto Alcan	Canada	Frank R. Feret
Slovalco a.s. Dept Laboratories	Slovakia	Jozef Lovcican
TALUM, d.d.	Slovenia	Majda Rola, Goran Abramovic
Alufluor AB	Sverige	Mikael Tegnér
Alcoa aluminio S.A. - AlF3	Brazil	Paulo Henrique B Martinez
Corporation Scientifique Claisse	Canada	C. O. Arsenault
Tanfac Industry	India	

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ILS

Samples were shipped early May 2009.

Samples were from Do-Fluorides, Boliden Odda, Fluorsid and Hydro Porsgrunn referenced stock (Norzink 2005 and a Derivados del Fluor AlF_3 used at Rheinwerk 2006) .

Return of results was June 20th

All participants returned results in time.

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Reported Elements

O	2
F / AlF3	7
Na	10
Mg	1
Al	4
Si	11
P	11
S	10
Ca	8
Fe	11
Zn	2
Ga	1
As	2
Pb	2

The selected elements had sufficient results to be included in the precision data treatment.

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ILS - Precision

Precision is two-fold

- **Within-laboratory repeatability, r**
- **Between-laboratory reproducibility, R**

The statistical treatment was done using ASTM E691; r & R are calculated to 95% confidence level.

Example: AlF_3 from F.

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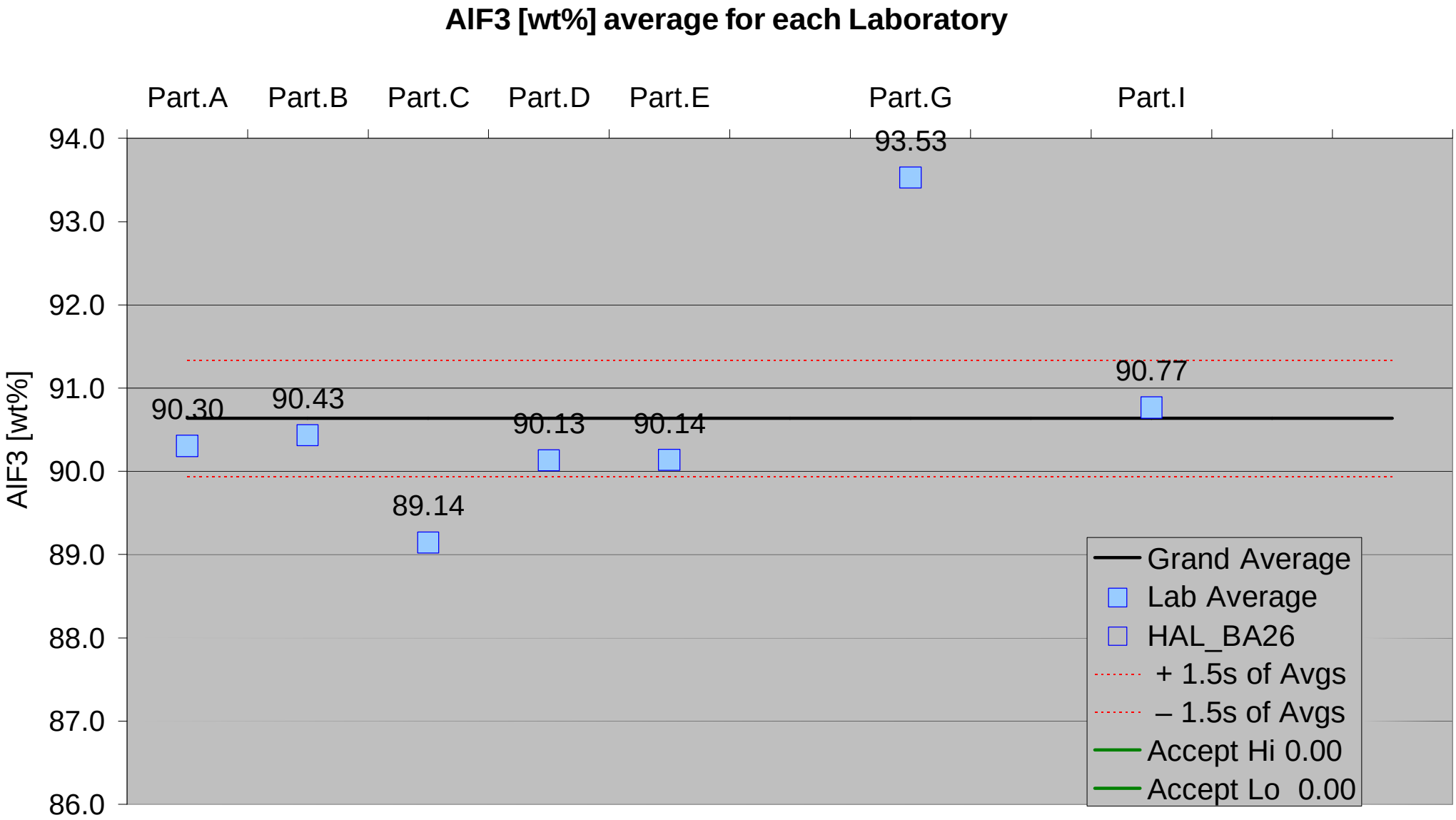
Evaluating Results - 1



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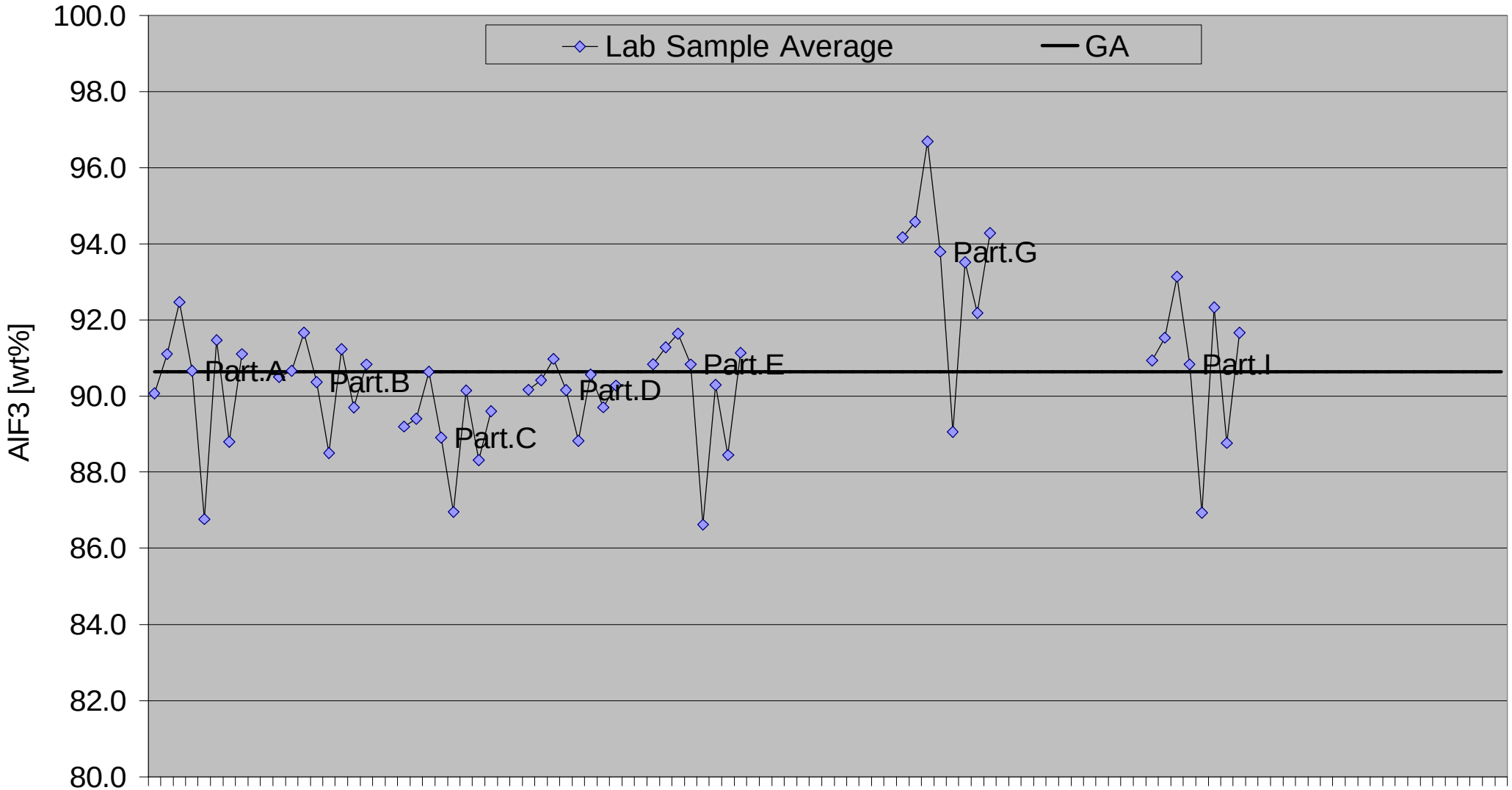
Evaluating Results - 2

Figure 00-A - AlF3 [wt%] Laboratory's Samples Average



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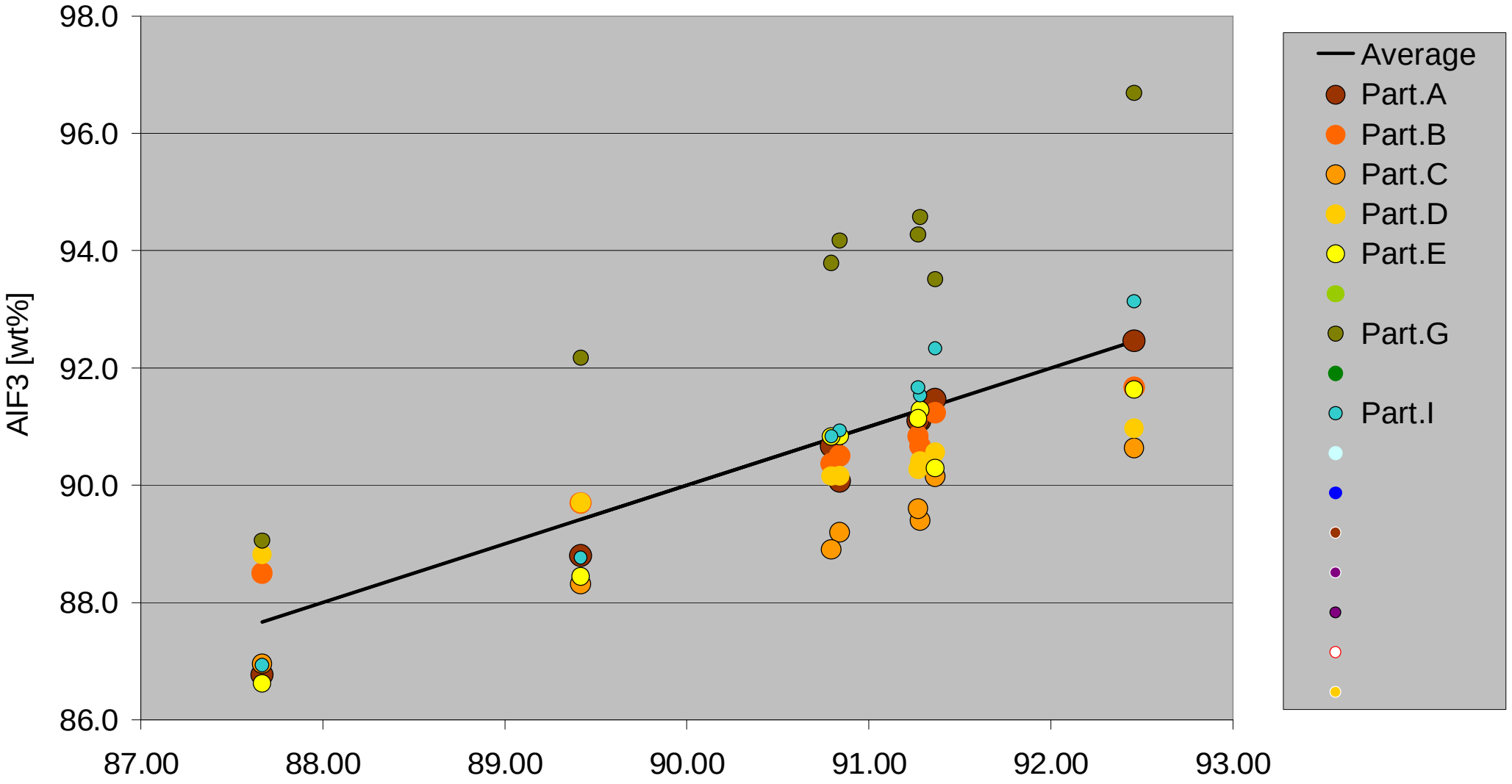
Evaluating Results - 3

Figure 00-B - Trend AlF3 [wt%] of each Laboratory vs. average trend



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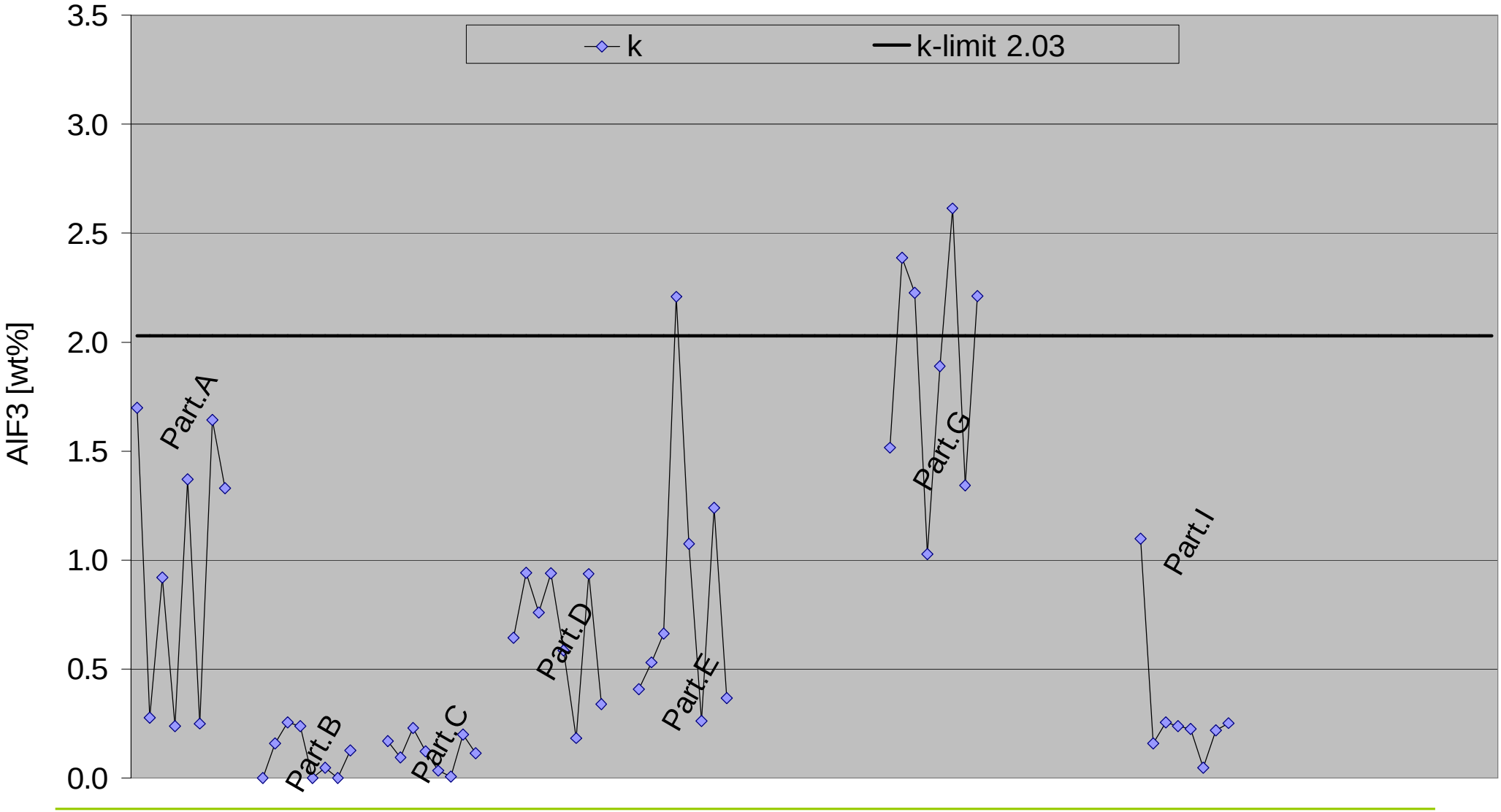
Evaluating Results - 4

Figure 00-C - AlF3 [wt%] - Within-Lab Consistency k by Laboratory



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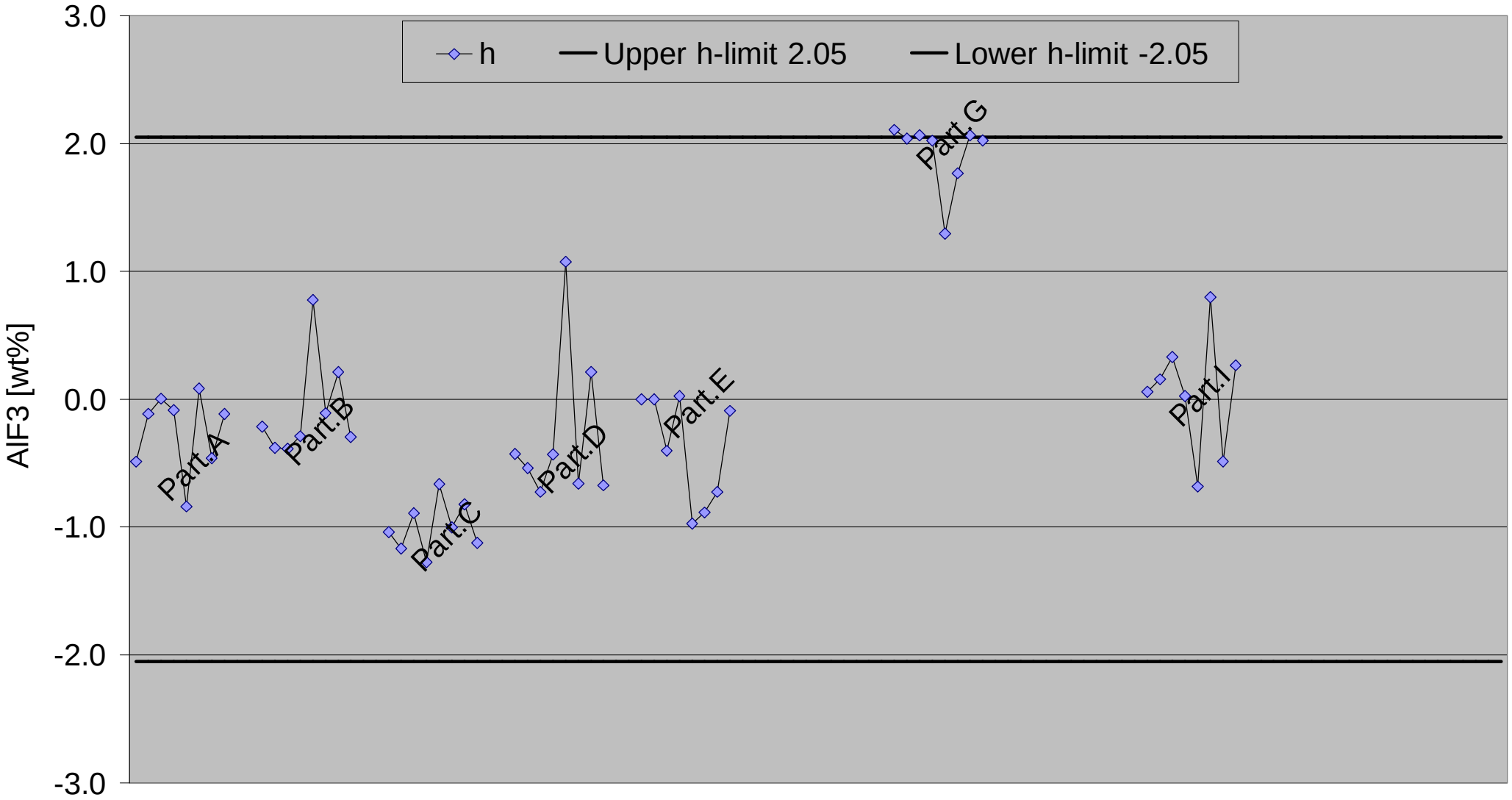
Evaluating Results - 5

Figure 00-D - AlF3 [wt%] - Between-Lab Consistency h by Laboratory



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Evaluating Results - Actions

First evaluation:

AlF_3 [wt%] - Repeatability Limit, r = 1.2 wt%

AlF_3 [wt%] - Reproducibility Limit, R = 4.3 wt%

ACTION 01 – Part.I determination used an alternative analysis so the results were removed, number of laboratories decreased by 1.

ACTION 02 - Inconsistency in r&R – Part.G showed high k-values and high h-values - each determination was replaced with the average of other laboratories and the number of laboratories decreased by 1.

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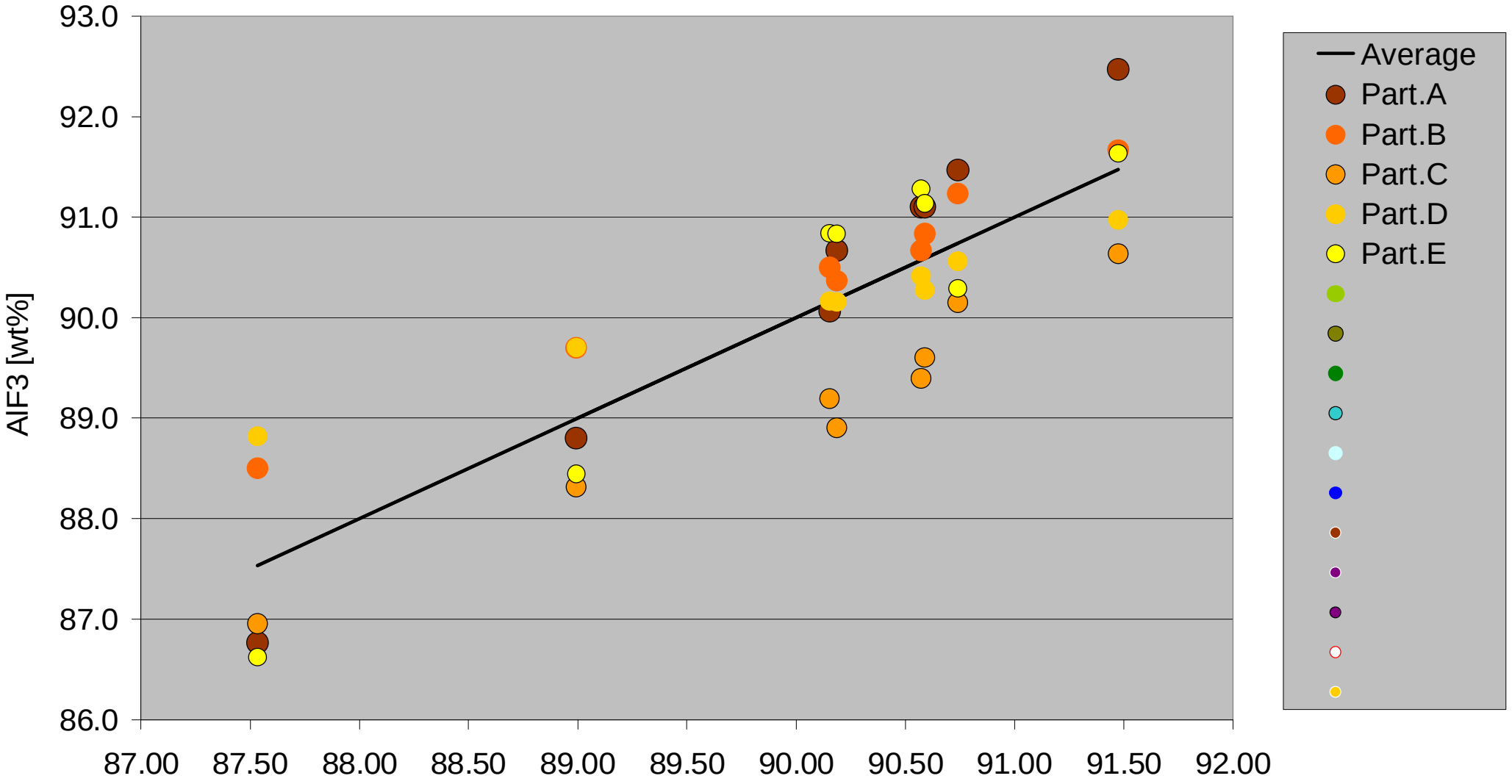
Evaluating Results - 6

Figure 02-B - Trend AlF3 [wt%] of each Laboratory vs. average trend



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Evaluating Results - Actions

Final evaluation:

AlF_3 [wt%] - Repeatability Limit, r = 0.6 wt%

AlF_3 [wt%] - Reproducibility Limit, R = 2.1 wt%

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F/AlF_3 Precision Statement

The precision statement is valid in the aluminium fluoride concentration range 86.5 to 93.5 wt%. The aluminium fluoride level should be reported in weight percent with one decimal.

WITHIN-LAB: Given a determination at the same laboratory of two test portions of the same material separately prepared within a short time by the same operator, the difference between the two measurements should be within r = 0.6 wt% for 95 out of 100 such comparisons.

BETWEEN-LAB: Given the determination at two different laboratories of a test portion of the same material, the difference should be within R = 2.1 wt% for 95 out of 100 such comparisons.

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Results

Element	Range	r	R
AlF_3 from Fluorine, F	86.5-93.5	0.6	2.1
Sodium, Na	0.05-0.25	0.011	0.085
Silicon, Si	0.001-0.10	0.002	0.014
Phosphorus, P	0.001-0.020	0.0005	0.0026
Sulfur, S	0.01-0.60	0.006	0.063
Calcium, Ca	0.001-0.10	0.004	0.011
Iron, Fe	0.005-0.05	0.0014	0.0022

Committee Draft

ISO CD 12926-1 () — Aluminium fluoride primarily used for the production of aluminium — Determination of elements — Wavelength dispersive X-ray fluorescence spectrometric method — Part 1: Method using pressed powder tablets

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