



Waste Oil 2010 Round Robin

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SECIL, SA

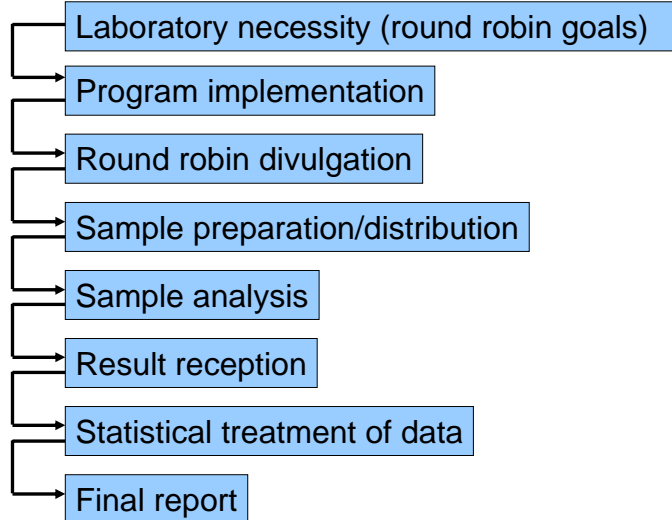


**“He who makes a mistake and does
not correct it is making another.”**

Confucius



Steps to organize a round robin



Oily sludge

- Hydrocarbons and water;
- No round robins for this type of fuel;
- No reference material available;
- Difficult analysis;
- Samples with great heterogeneity.



Goals of the round robin trial

- Collect data to method validation (accreditation process);
- Create an internal reference material (IRM);
- Performance evaluation for the laboratory;
- To create cooperative relations between laboratories.



Proposed program

- Participation was opened for any laboratory;
- Participants received 3 samples from different origins;
- Proposed determinations:

Group	Parameter
General analysis	Water content, calorific value
Elementary analysis	Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S)

- Possibility to add new analysis if there where a minimum of 8 participants interested.



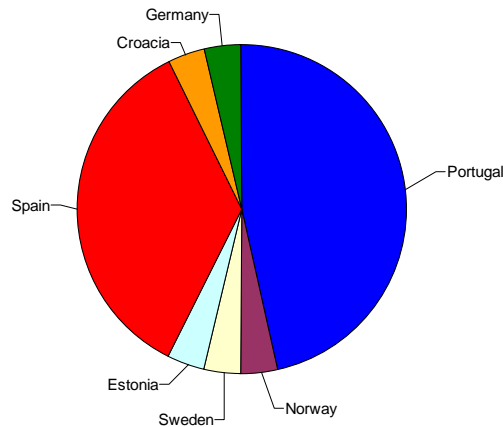
Sample preparation

- Samples obtained directly from trucks
- Physical homogenization of samples
- Similar portions distributed for each participant



Participants

Forschungsinstitut der Zementindustrie GmbH	Laboratório de Análises – IST
Nasicecement d.d.	Laboratório Central do Grupo CIMPOR
Compañía Española de Petroleos, SA	Lab. Análises Químicas da TecMinho
Fundación Tekniker	LNEG – UEZ
Ambitec Laboratorio MedioAmbiental S.A	Sisav
Alquimia Soluciones Ambientales	Ecodeal
(Intertek) Asociacion BTC	Carmona
Agència de Residus de Catalunya	Lab. de Combustíveis do LNEG
SGS Española de Control S.A.	LCR - Lab de Caracter. de Resíduos
Lab. de Ensayo de Combustibles – Biolar	Secil - CMP - Fábrica Cibra-Pataias
Dep. de Edafología y Química Agrícola	Secil - CMP - Fábrica Maceira-Liz
Repsol Petroleo S.A.	Secil Outão
Kunda Nordic Cement Corp.	Citri
Renor Brevik	Cementa AB - Cementa Research AB



Portugal	13
Norway	1
Sweden	1
Estonia	1
Spain	10
Croatia	1
Germany	1
Total	28

■ Detection of outliers –Grubb's test

↳ Verification done to the maximum and minimum value in a group of determinations

1. Sort values in crescent order.
2. Calculate the Grubb's variable, G_p

$$G_p = \frac{(x_p - \bar{x})}{s}$$

x_p - largest value in group
 \bar{x} - the average of determinations
 s - standard deviation

3. Compare the obtained value with known Grubb's critical values



Grubb's test (cont.)

- a. Calculated $G_p < 5\%$ critical value – not an outlier;
 - b. 5% critical value $<$ calculated $G_p < 1\%$ critical value – straggler;
 - c. Calculated $G_p > 1\%$ critical value – outlier.
4. If straggler or outlier is detected then value eliminated from the data set;
 5. Afterwards smallest value in data set is also tested using the same method:

$$G_1 = \frac{(\bar{x} - x_1)}{s}$$

x_1 - smallest value in group
 \bar{x} - the average of determinations
 s - standard deviation

6. After eliminating all values the average of the remaining is considered the true value



Performance evaluation

- For each laboratory a performance value is determined, Z-score:

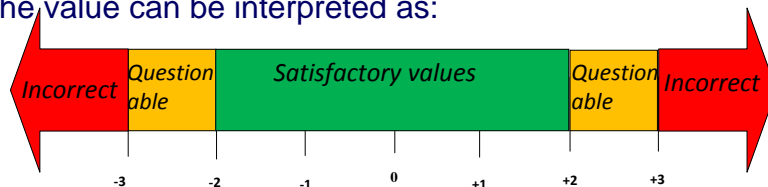
$$Z = \frac{(X_{lab} - X_v)}{s}$$

X_{lab} – value determined for each lab.

X_v – true value determined.

s – standard deviation

- The value can be interpreted as:





Registration vs. results obtained

- From a total of 28 registered laboratories

Samples	Determination					
	Water content	Calorific value	Carbon	Nitrogen	Hydrogen	Sulphur
1/2/3	24	25	18	16	16	24

- Number of results obtained in each determination

Samples	Determination					
	Water content	Calorific value	Carbon	Nitrogen	Hydrogen	Sulphur
1	16	17	13	12	12	15
2	15	16	13	12	12	14
3	16	17	13	12	12	15



Results

Why some laboratories could not report a result:

- Results below the quantification limit;
- Results not trustworthy;
- Problems with the analysis equipments;
- Equipments are not ready to analyze this type of samples.

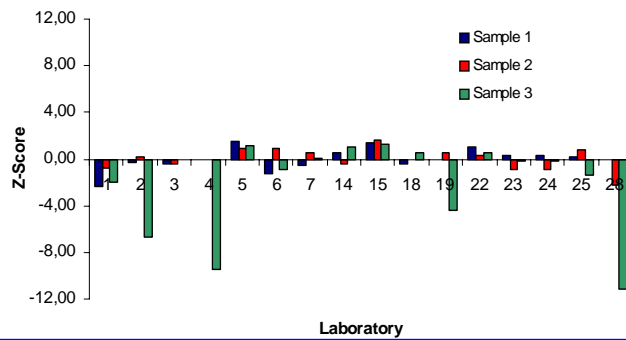
Other problems encountered by laboratories:

- Samples extremely heterogeneous;
- Unable to fully homogenize samples.



Water content

Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	16	14	86	5
2	15	14	53	22
3	16	12	88	8



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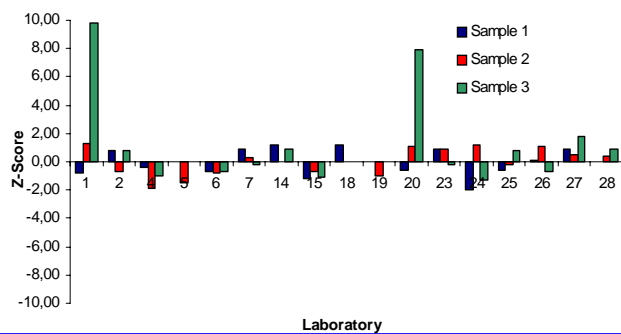
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Calorific value

Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	17	14	2748	1392
2	16	16	16838	8518
3	17	12	2876	2073



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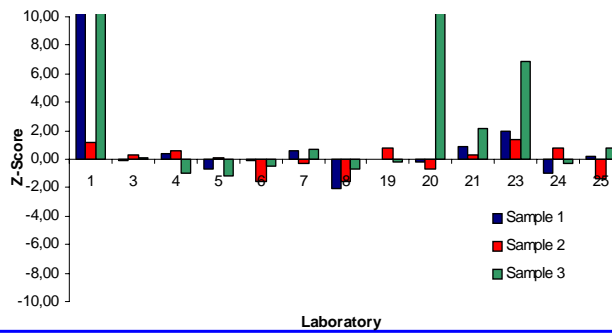
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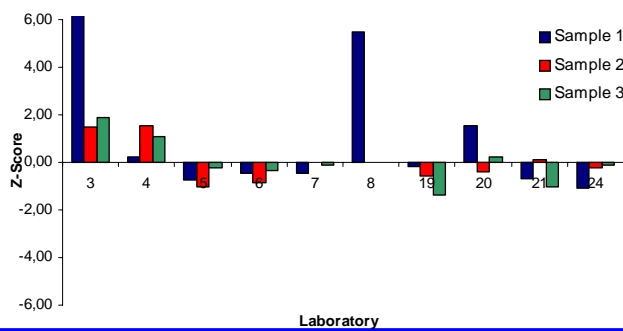
Carbon

Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	13	12	7,3	2,6
2	13	13	37,2	18,3
3	13	10	4,7	1,8



Nitrogen

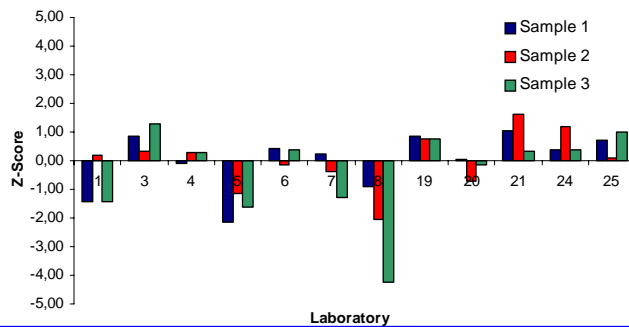
Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	12	8	0,23	0,03
2	12	8	0,18	0,06
3	12	9	0,31	0,10





Hydrogen

Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	12	12	9,95	1,24
2	12	12	11,05	0,90
3	12	11	10,50	0,50



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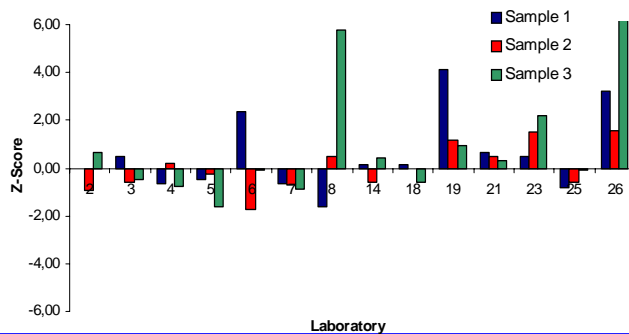
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Sulphur

Sample	Number of results	Number of valid results	Average (%)	Standard deviation (%)
1	15	12	0,20	0,06
2	14	13	0,58	0,20
3	15	12	0,08	0,04



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Critical points evaluation

Some of these points could influence result dispersion obtained:

- Sample preparation of vital importance;
- New laboratories that are not used to analyse these kind of samples;
- Samples almost with two distinct phases (necessity to homogenise samples prior analysing);
- Different determination methods used.



Conclusion

- Goal to obtain data for these samples was fulfilled – validation purpose;
- Necessity to form a new round robin panel to continue studying these heterogeneous samples;
- Thinking of doing a questionnaire to participants to analyze more thoroughly difficulties encountered.



Thank you for your attention

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