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National Physical Laboratory

PT Scheme for gas emissions monitoring
3rd Round

Review, Apr 2007, Bretby

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National Physical Laboratory

Introduction

- Review results from last round
- Discuss issues
- Feedback from participants
- Way forward
- Future PT workshops?

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Role of a PT scheme

- Provides a way to assess your own performance both against peers and against previous performance
- UKAS view PT schemes as a useful component of internal QA/QC
- Provides a focus to review and share best practice

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Scheme overview

- Organisation – STA
- Transport/ Logistics – Cryoservice
- NPL – determine gas concentrations referenced to primary standards
  - Gases from Cryoservice.
- Analysis - NPL

3rd Round

- 27 Participants
- Gases covered
  - Nominal concentrations
  - Actual concentrations were lower

Species	Nominal Concentration
SO_2 in Nitrogen	1000 ppm and 100 ppm
CO in Nitrogen	950 ppm and 85 ppm
NO in Nitrogen	450 ppm
O_2 in Nitrogen	11 %
Propane	9 ppm

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Assigned values

- Many PT schemes will use the average values of all participants results (after excluding outliers) as the assigned value for the samples
- We have an advantage as we can determine the value of the samples in a traceable way, and (hopefully) they won't change during the measurements.
- NPL measure the cylinders before the round and again at the end, traceable to our Primary National standards.
- The values we assign are not full certificates, and have a nominal uncertainty of 1%
- Cylinder values haven't changed during the round, generally better agreement than the 1% assigned uncertainty.
- Another QA check carried out is to check that no single cylinder gave significantly biased readings from all participants who measured it

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Traceable Gas Standards at NPL

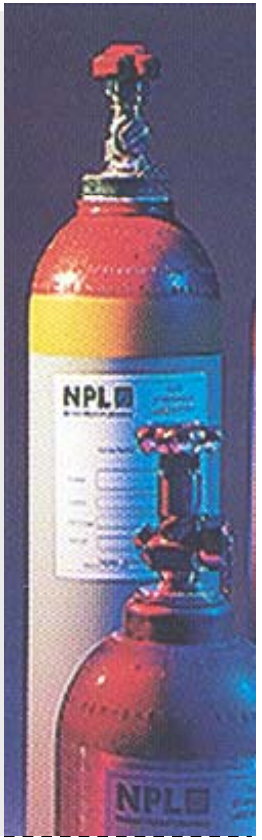
Primary Standard Gas Mixtures (PSM)
Concentration uncertainty ± 0.02% - 0.1%
at (95% level of confidence)

Primary Reference Gas Mixtures
Concentration uncertainty ± 0.1% - 0.4%
at (95% level of confidence)

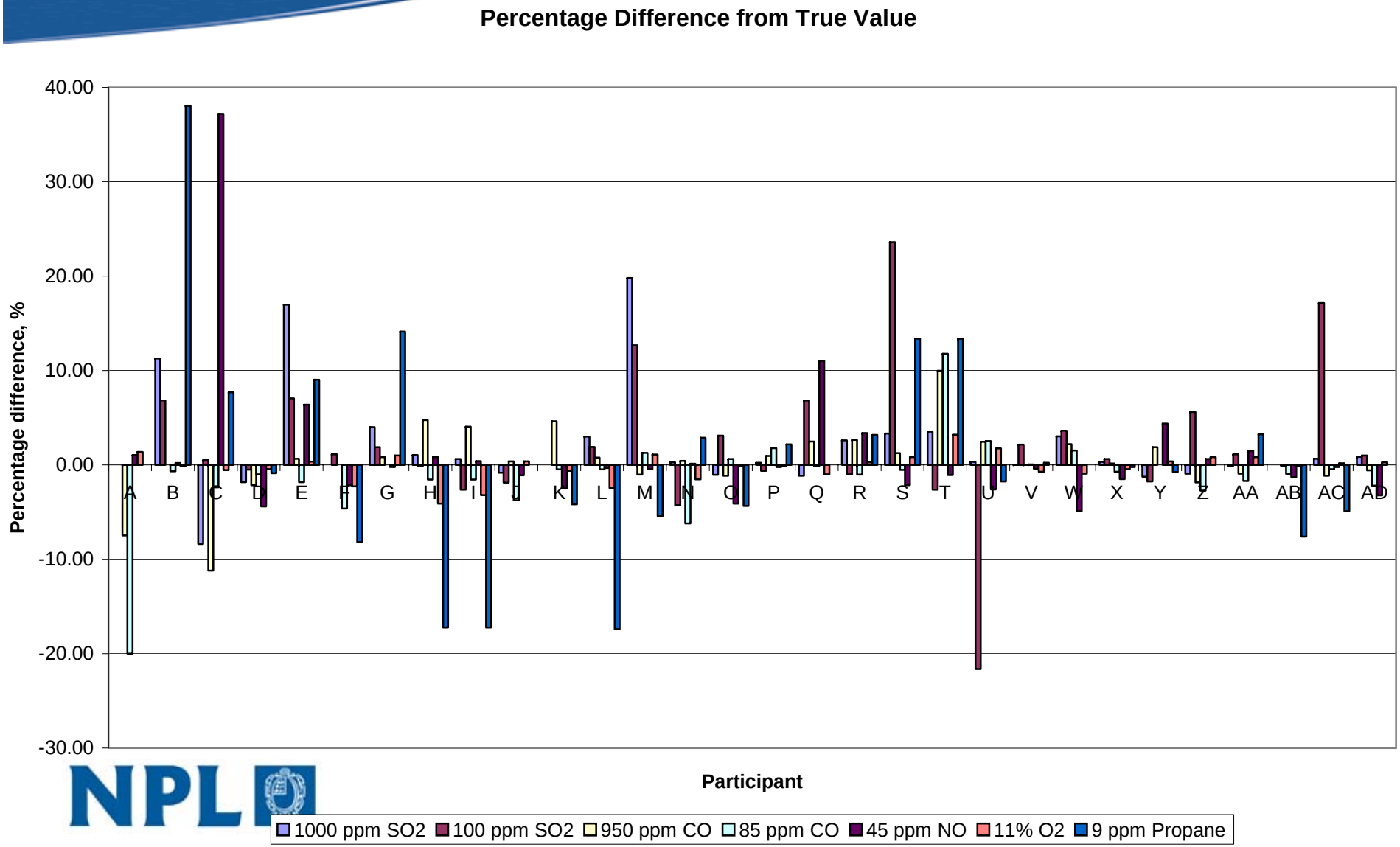
Secondary Gas Standards
Concentration uncertainty ±0.4% - 1%
at (95% level of confidence)

Certified Reference Gas Mixtures
Concentration uncertainty ±1% - 3%
at (95% level of confidence)

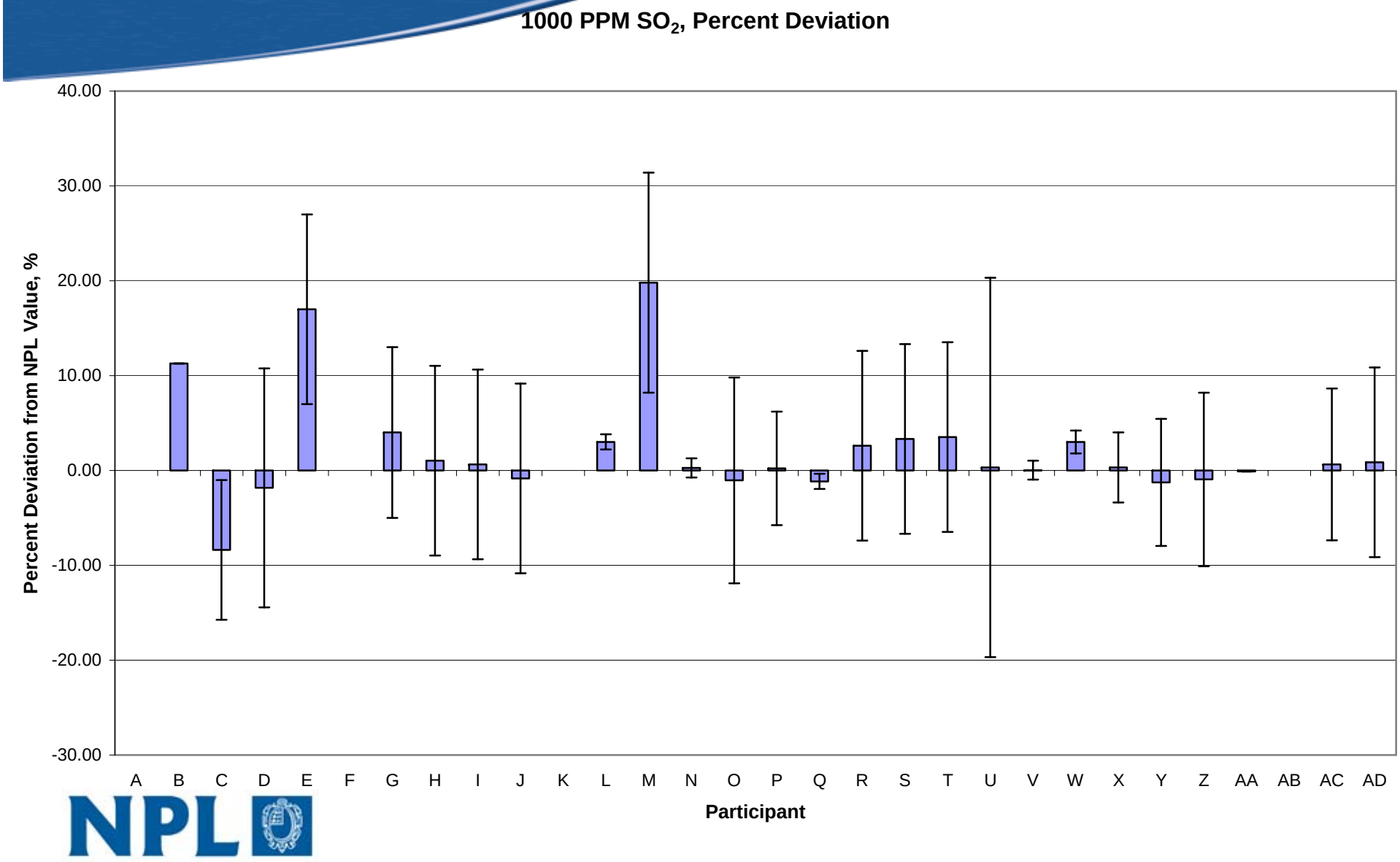
Dissemination to industry, Government laboratories and regulators



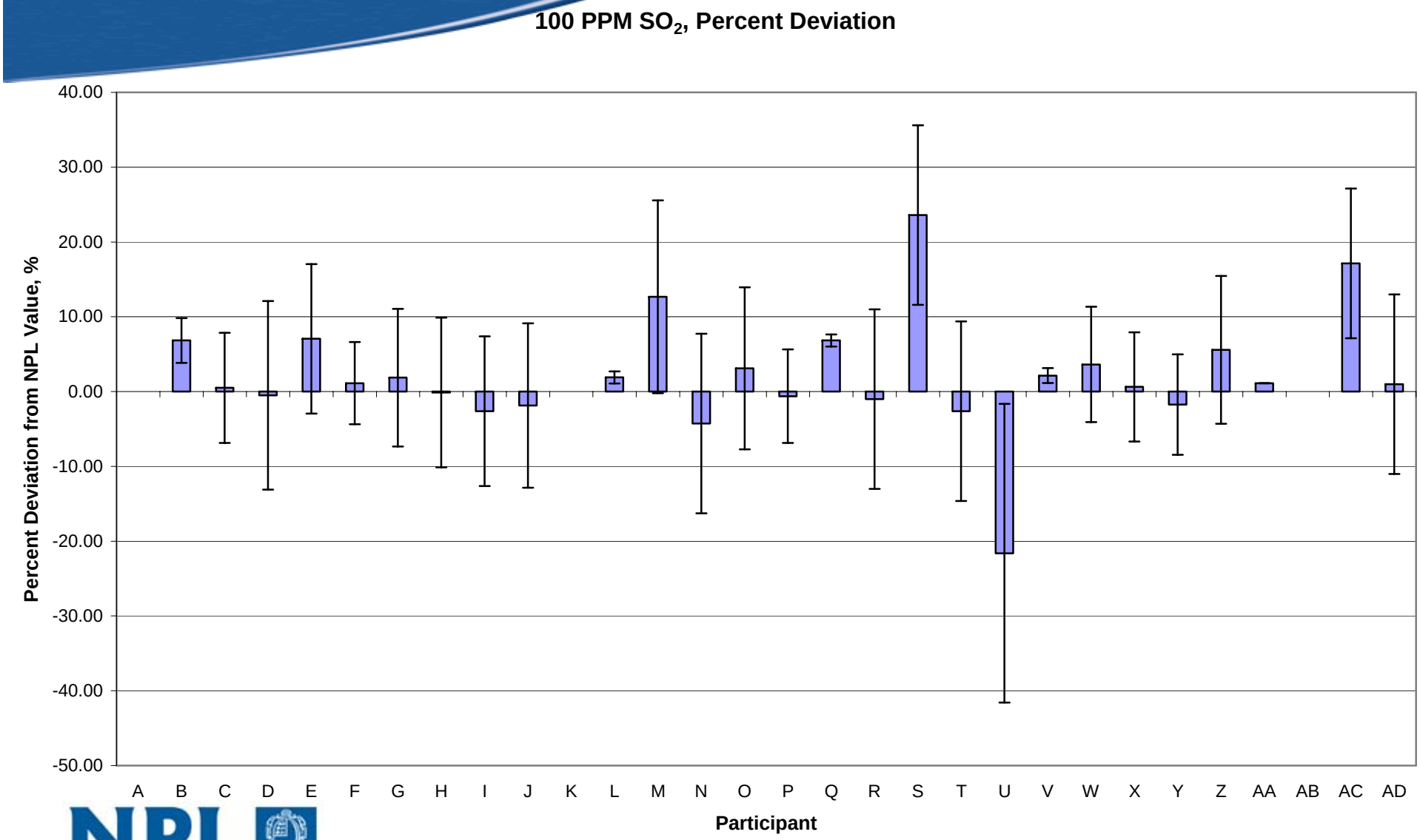
Overview of results



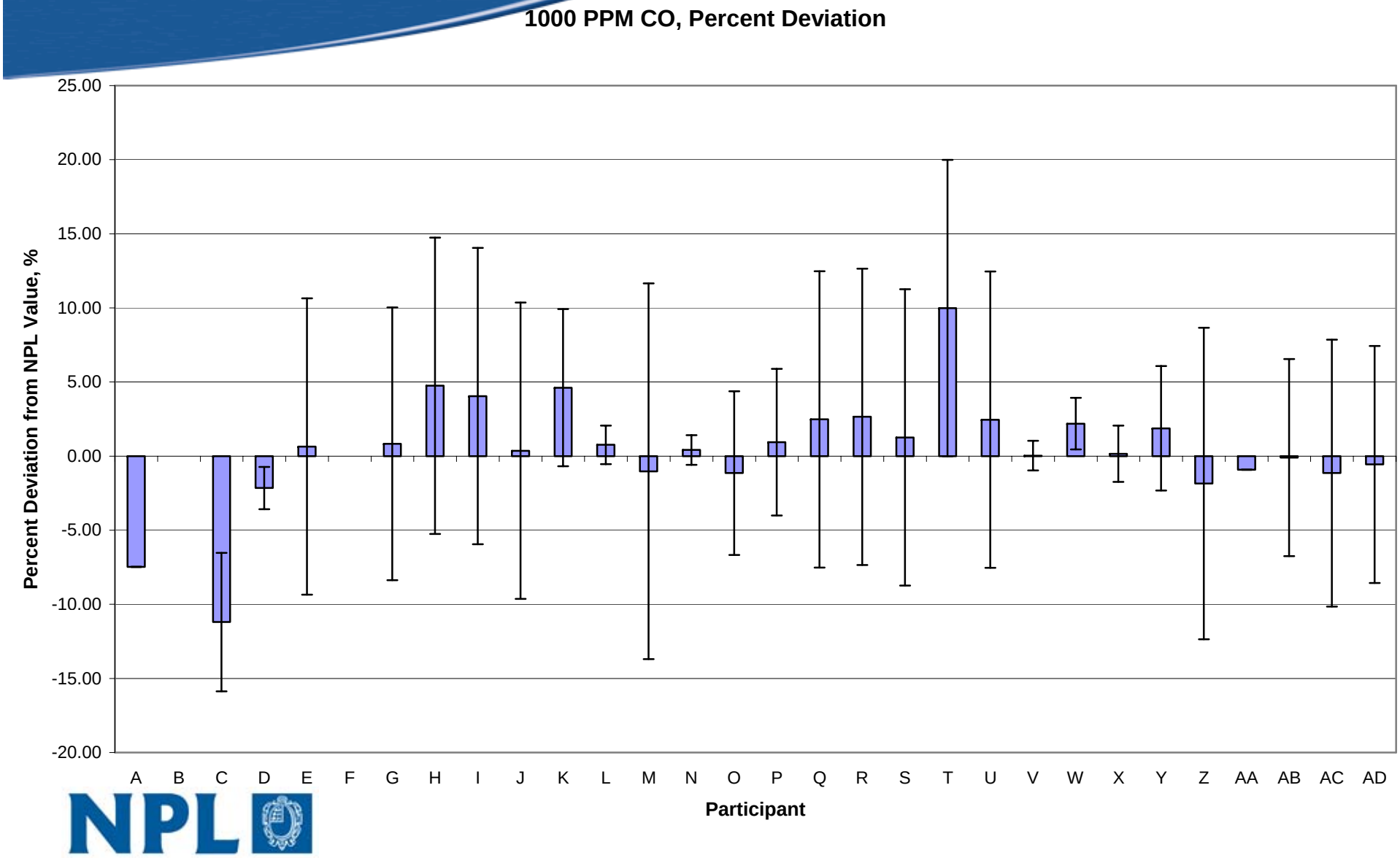
SO_2 1000 ppm


1000 PPM SO2, Percent Deviation
Percent Deviation from NPL Value, %
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

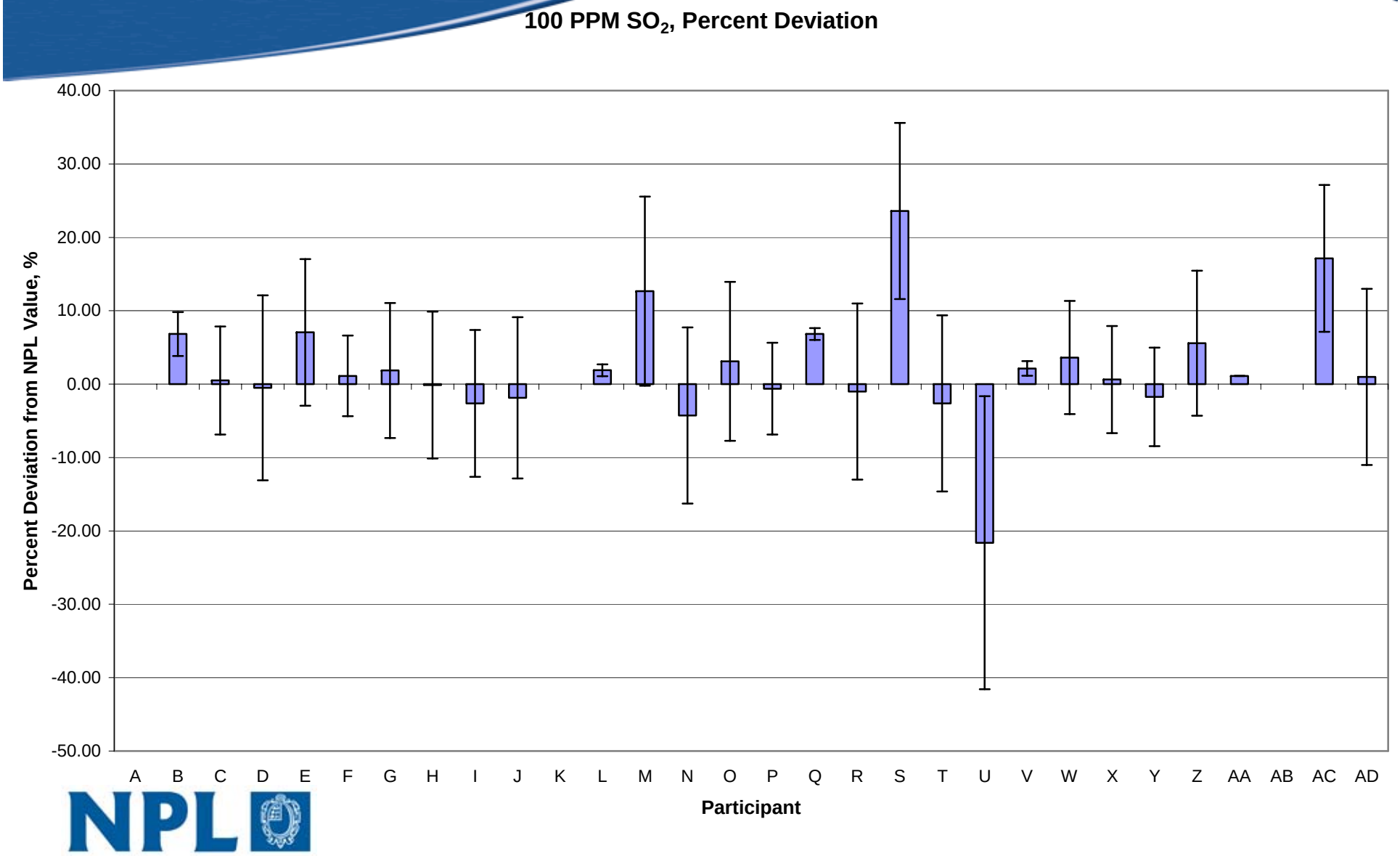
SO_2 100 ppm


100 PPM SO2, Percent Deviation
Percent Deviation from NPL Value, %
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
-40.00
-50.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

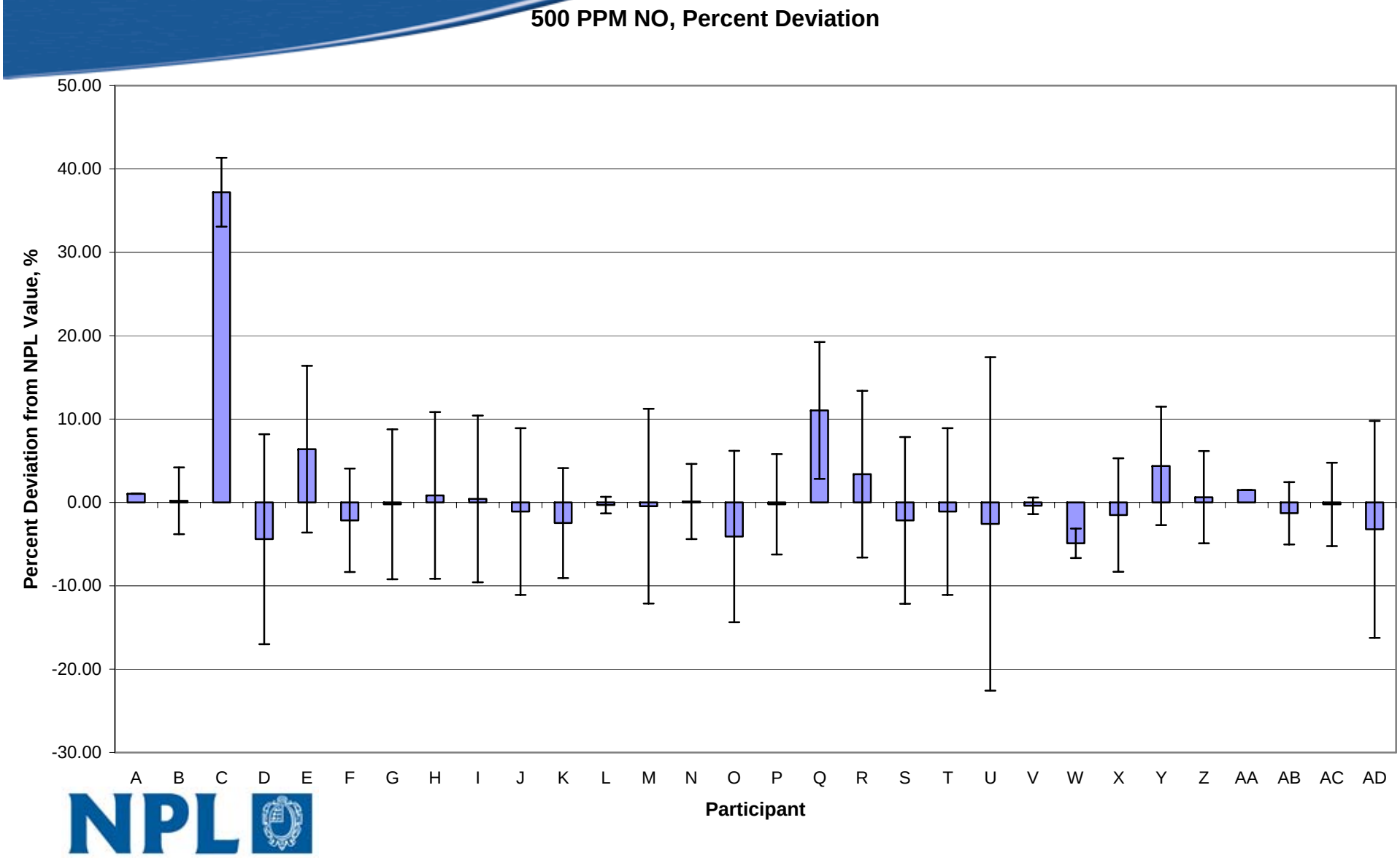
CO 1000 ppm


1000 PPM CO, Percent Deviation
Percent Deviation from NPL Value, %
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
-20.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

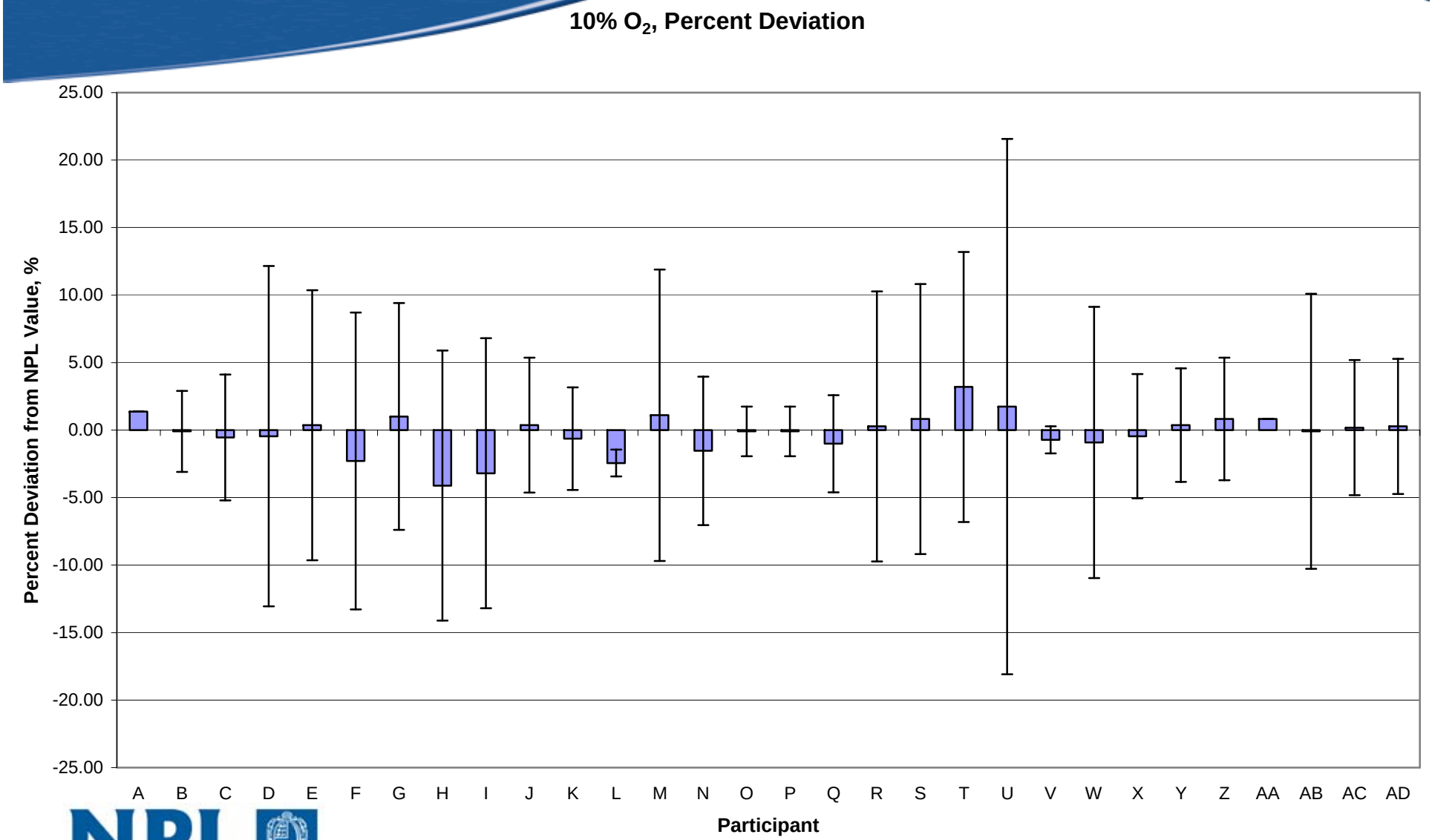
CO 100 ppm


100 PPM SO_2, Percent Deviation
Percent Deviation from NPL Value, %
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
-40.00
-50.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

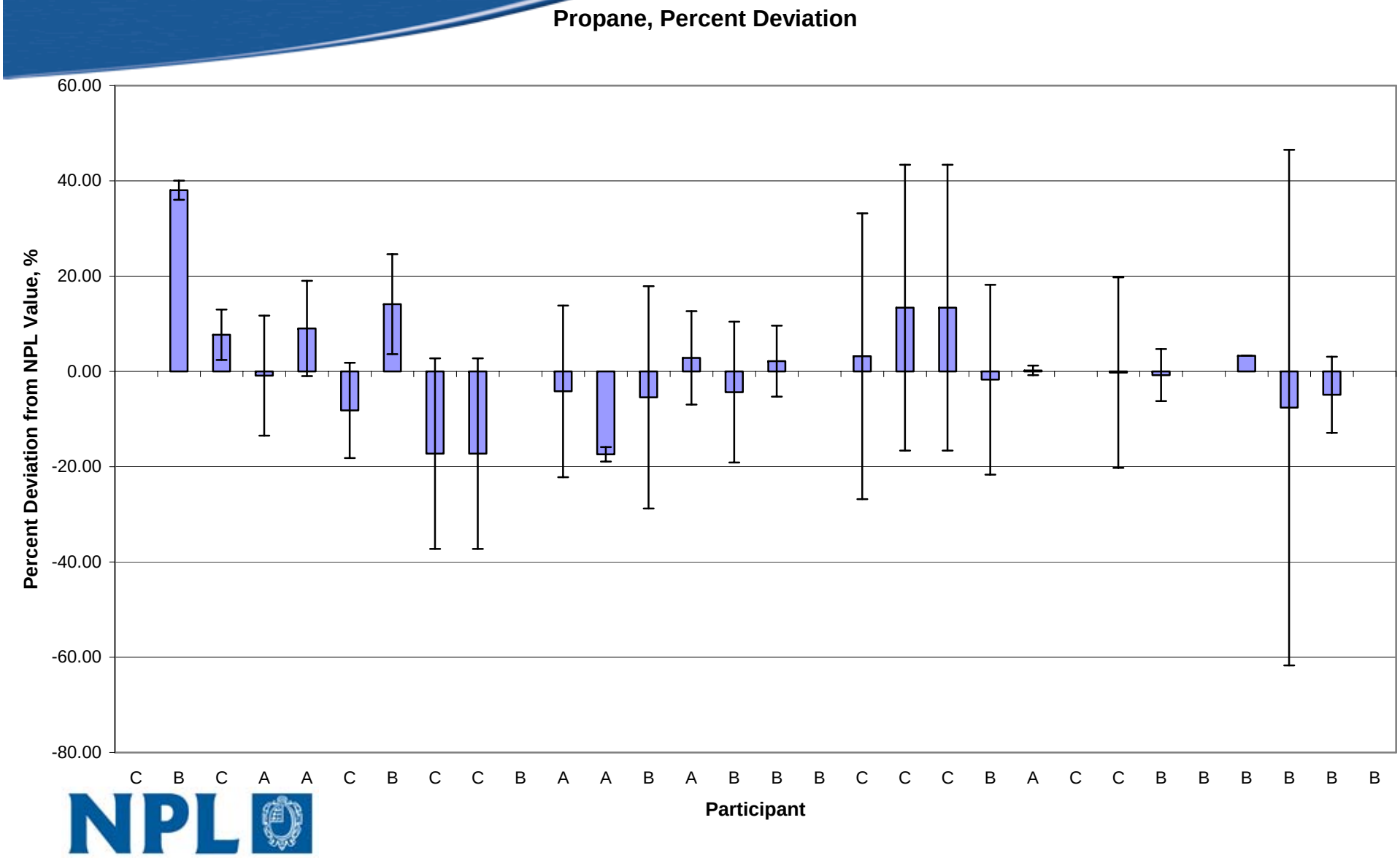
NO 500 ppm


500 PPM NO, Percent Deviation
Percent Deviation from NPL Value, %
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

O_2 10%


10% O2, Percent Deviation
Percent Deviation from NPL Value, %
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
-20.00
-25.00
A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA AB AC AD
Participant

Propane


Propane, Percent Deviation
Percent Deviation from NPL Value, %
60.00
40.00
20.00
0.00
-20.00
-40.00
-60.00
-80.00
C B C A A C B C C B A A B A B B B C C C B A C C B B B B B B
Participant

Z Scores

- Z Scores provide a way of normalising PT scheme results to allow comparison against a measurement requirement
- Z score is simply the ratio of a individual results deviation from the expected value divided by a target or expected deviation.
- What do we use as the target value
  - Decided to use the round one average deviations
  - Can also look at the scores with respect to the requirements of the directives.
    - However measurement of a gas cylinder should be much better than this

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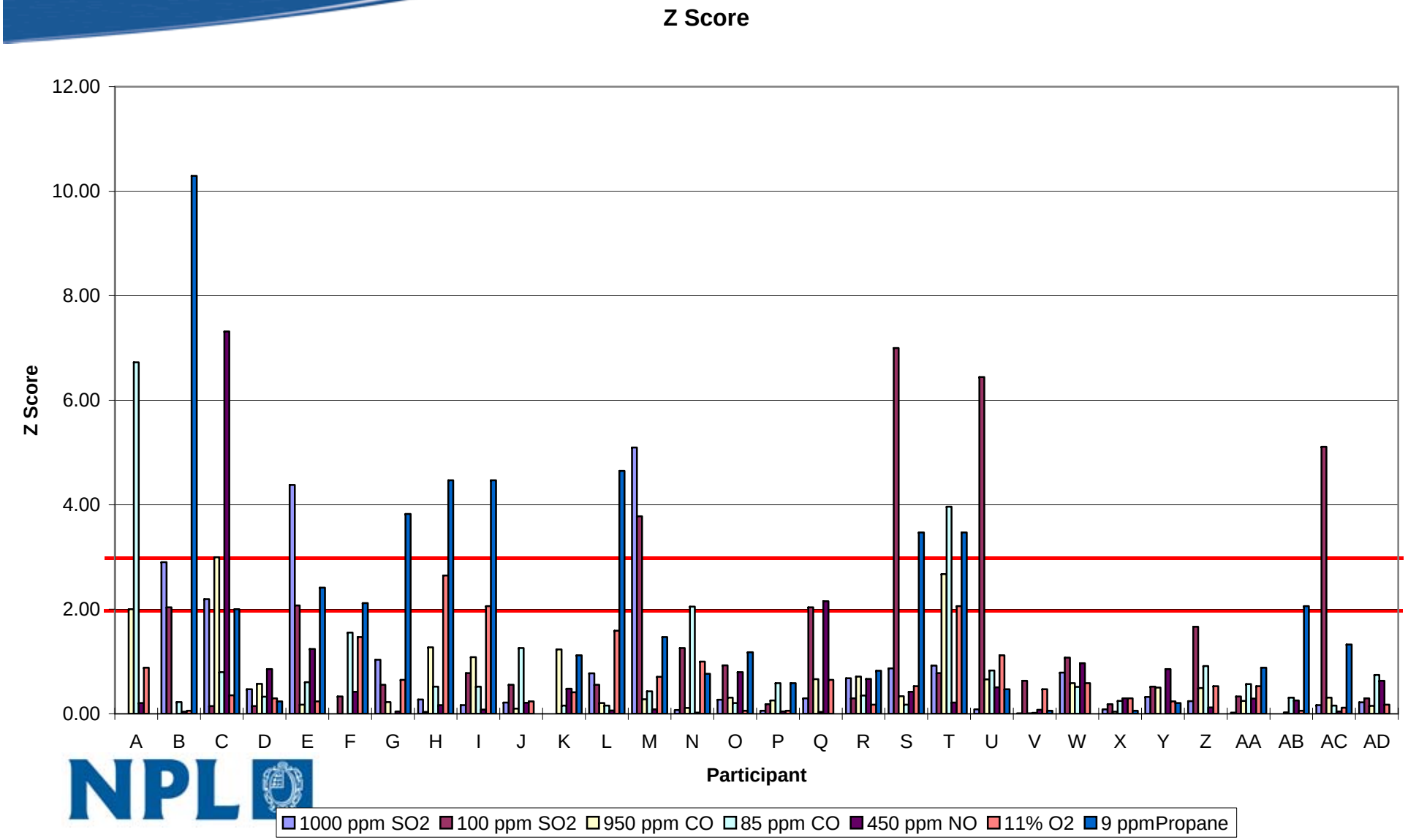
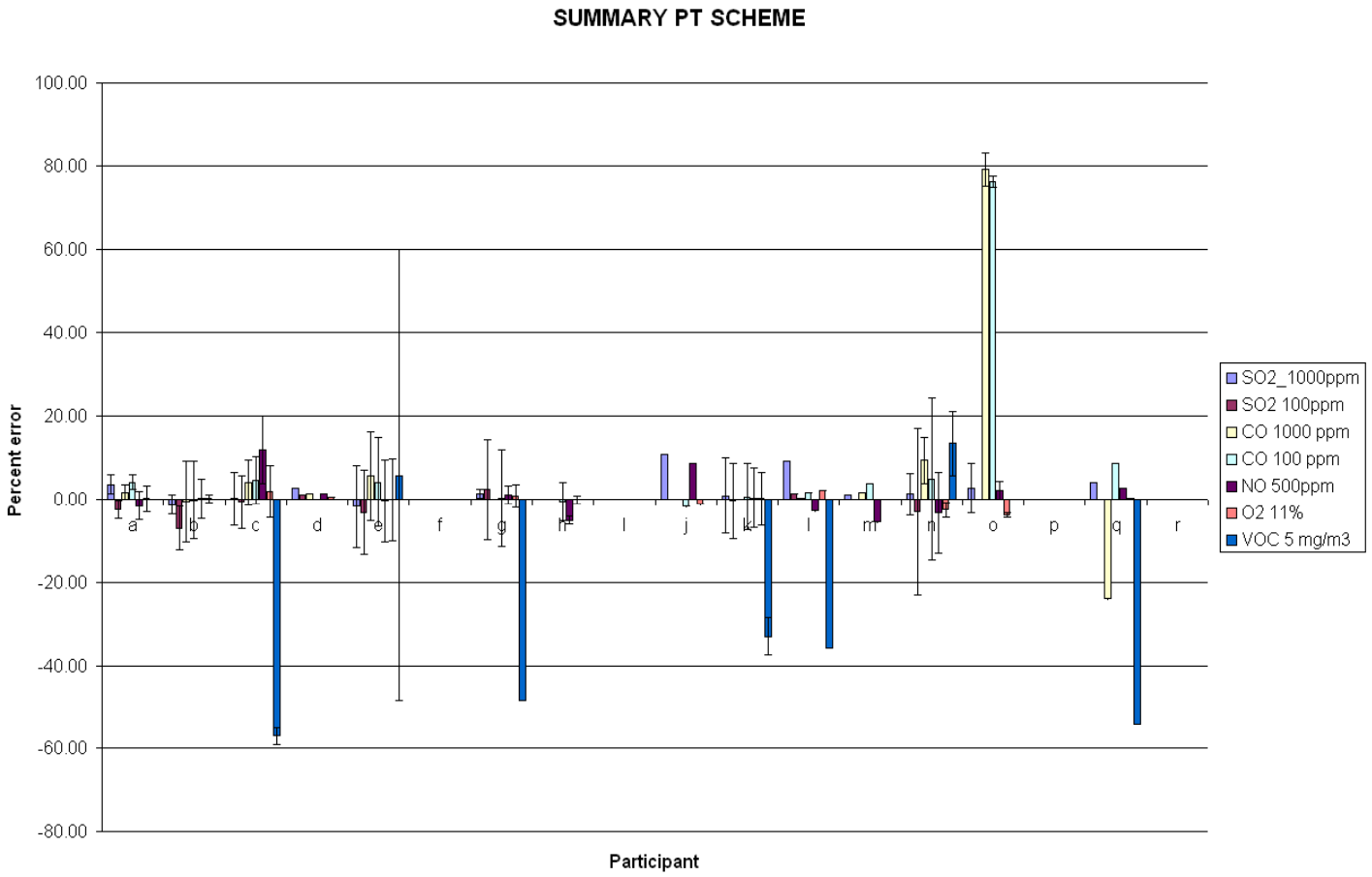
Target deviations

- Target deviation as percentage
  - CO 3.5%
  - NO 5.5 %
  - O_2 1.7 %
  - SO_2 4 %
  - VOC 7 %

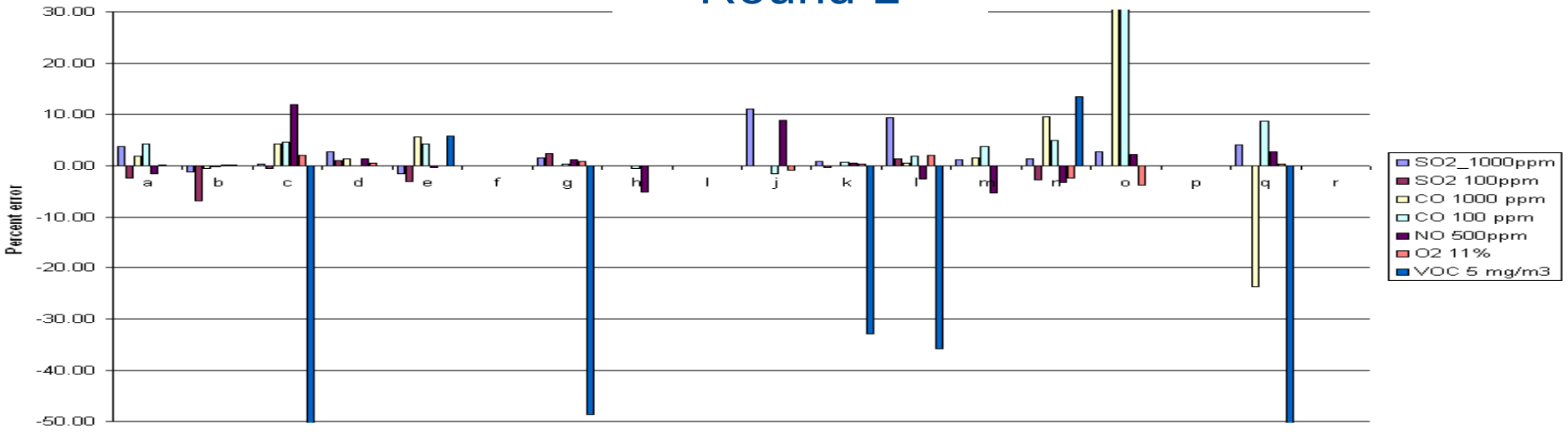
Overall Z scores



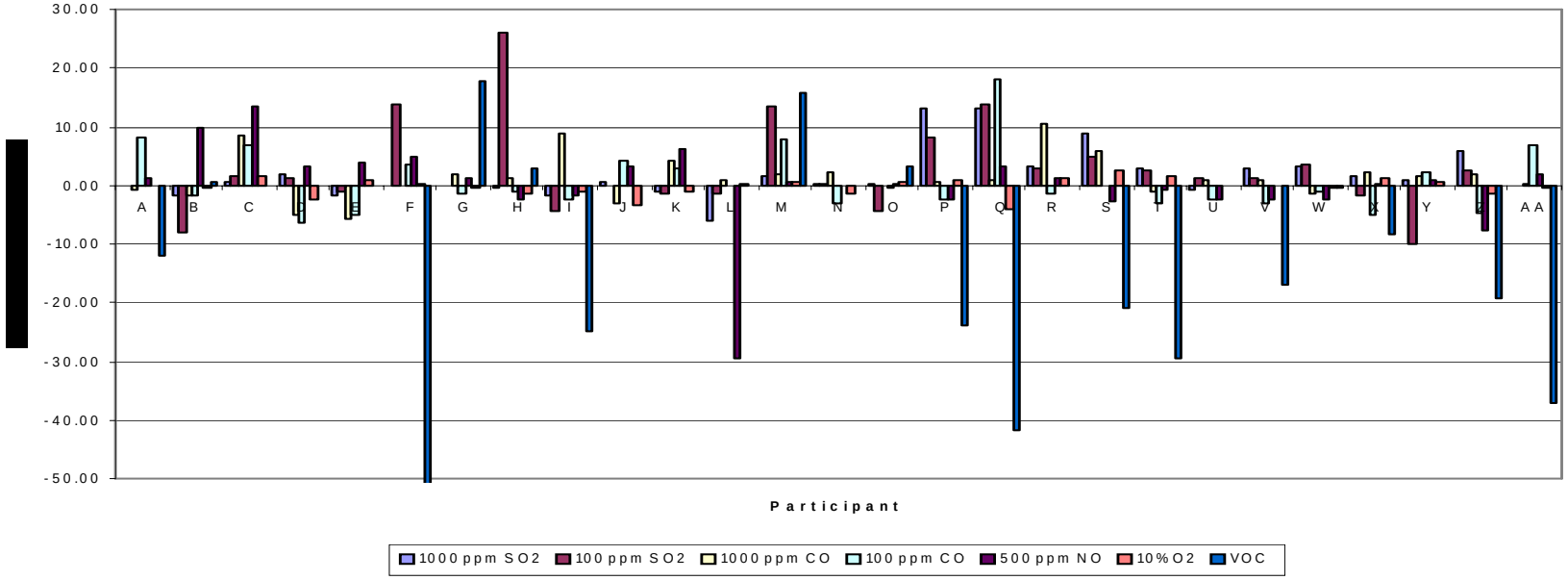
Round 1, percentage errors



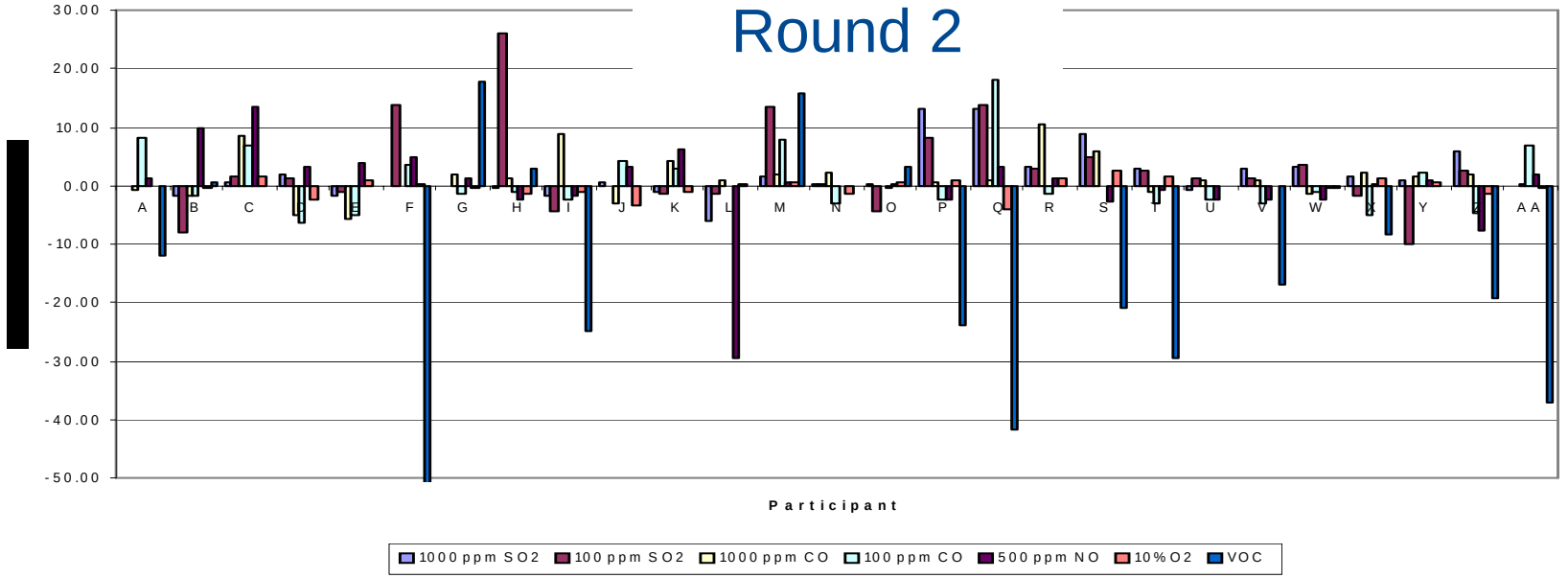
Round 1



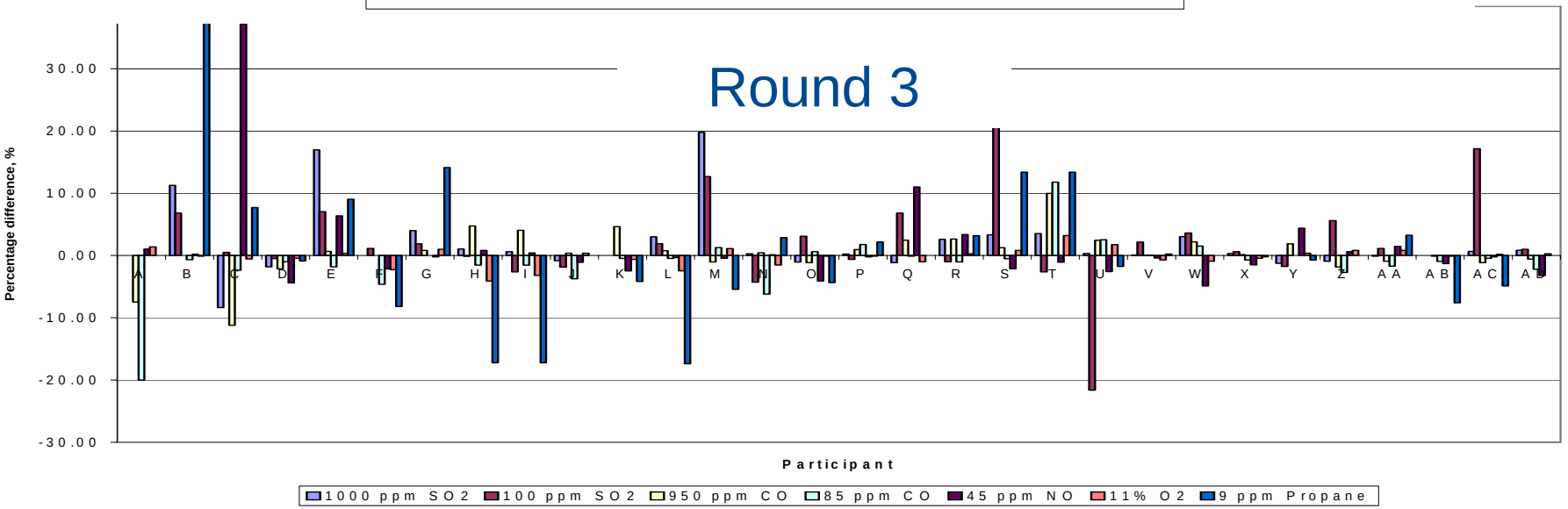
Round 2



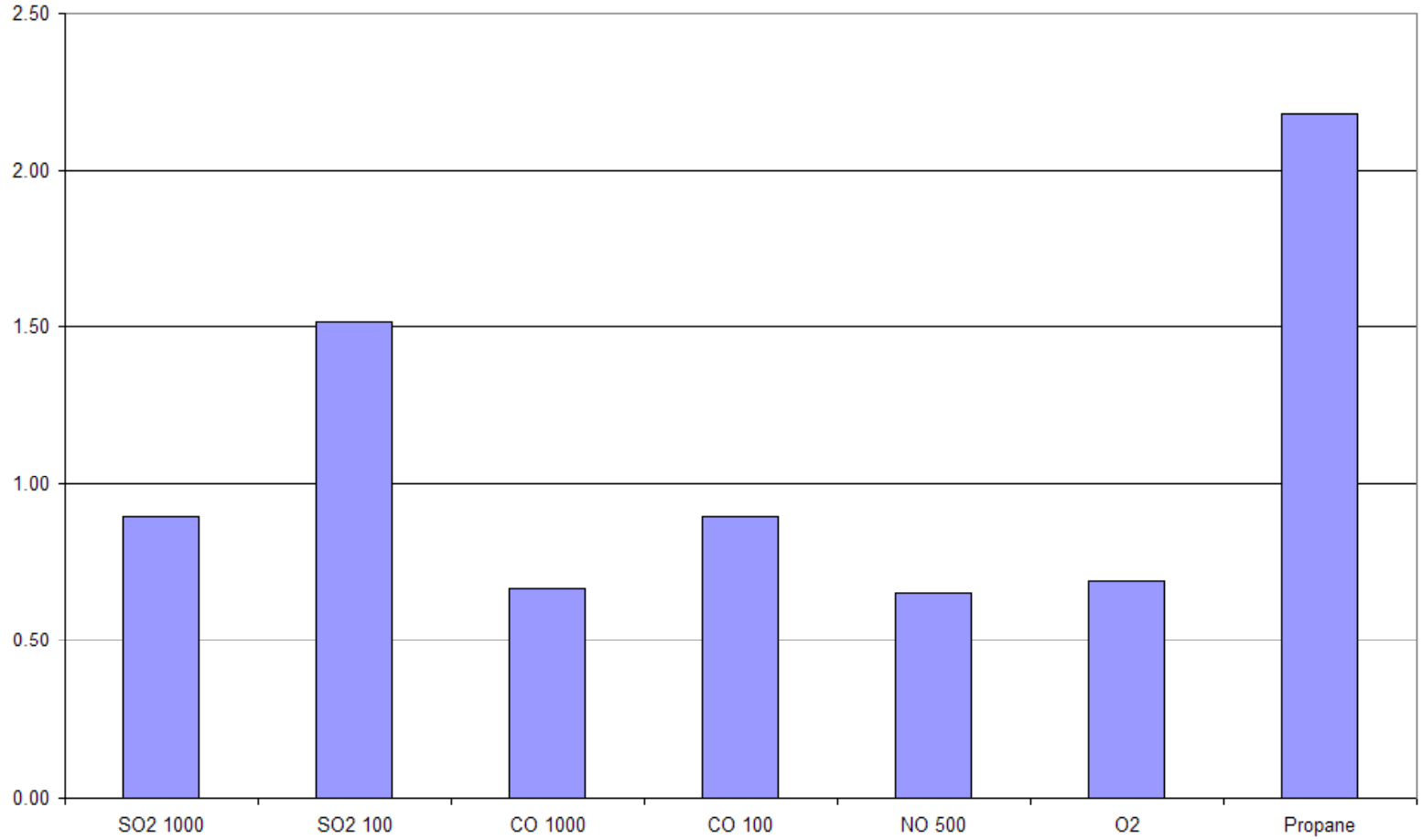
Round 2



Round 3



Average Z score grouped by gas



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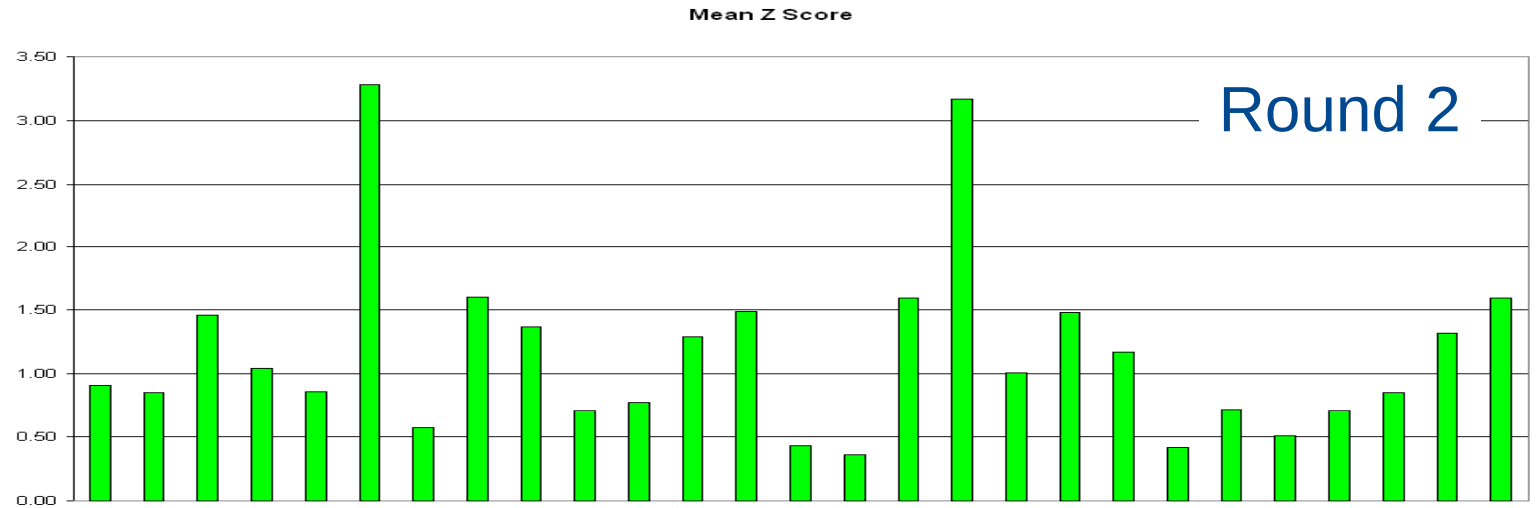
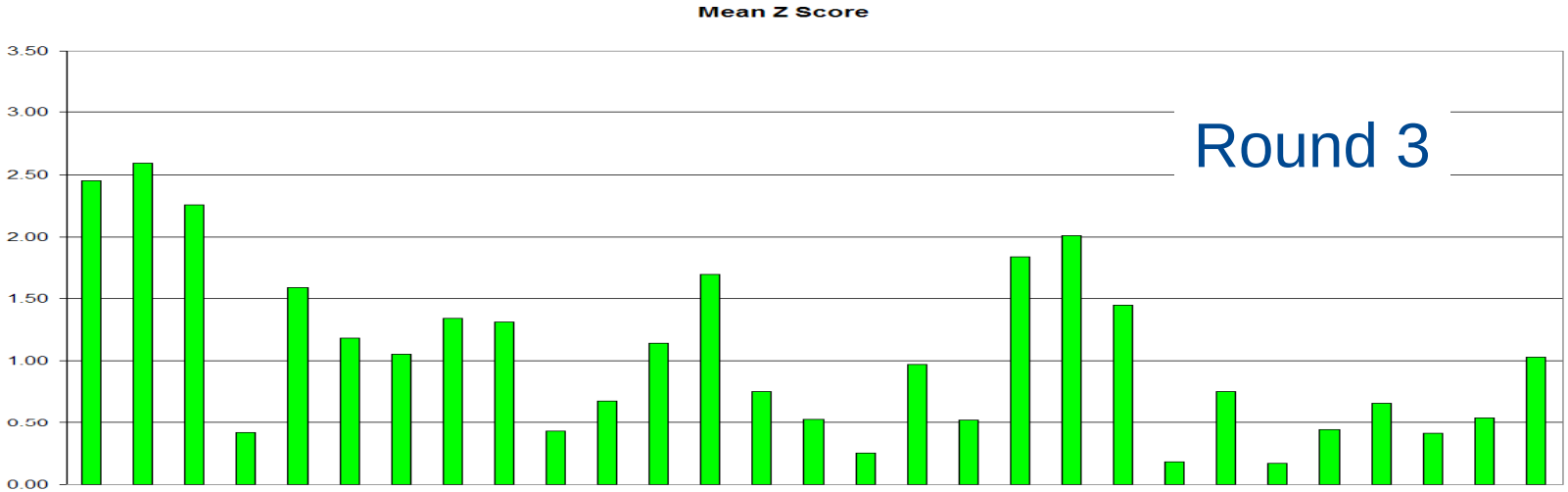
Mean z scores





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Comparison with previous rounds

- All participants had mean z scores better than 3
  - This implies they are performing better than the average performance in the previous round

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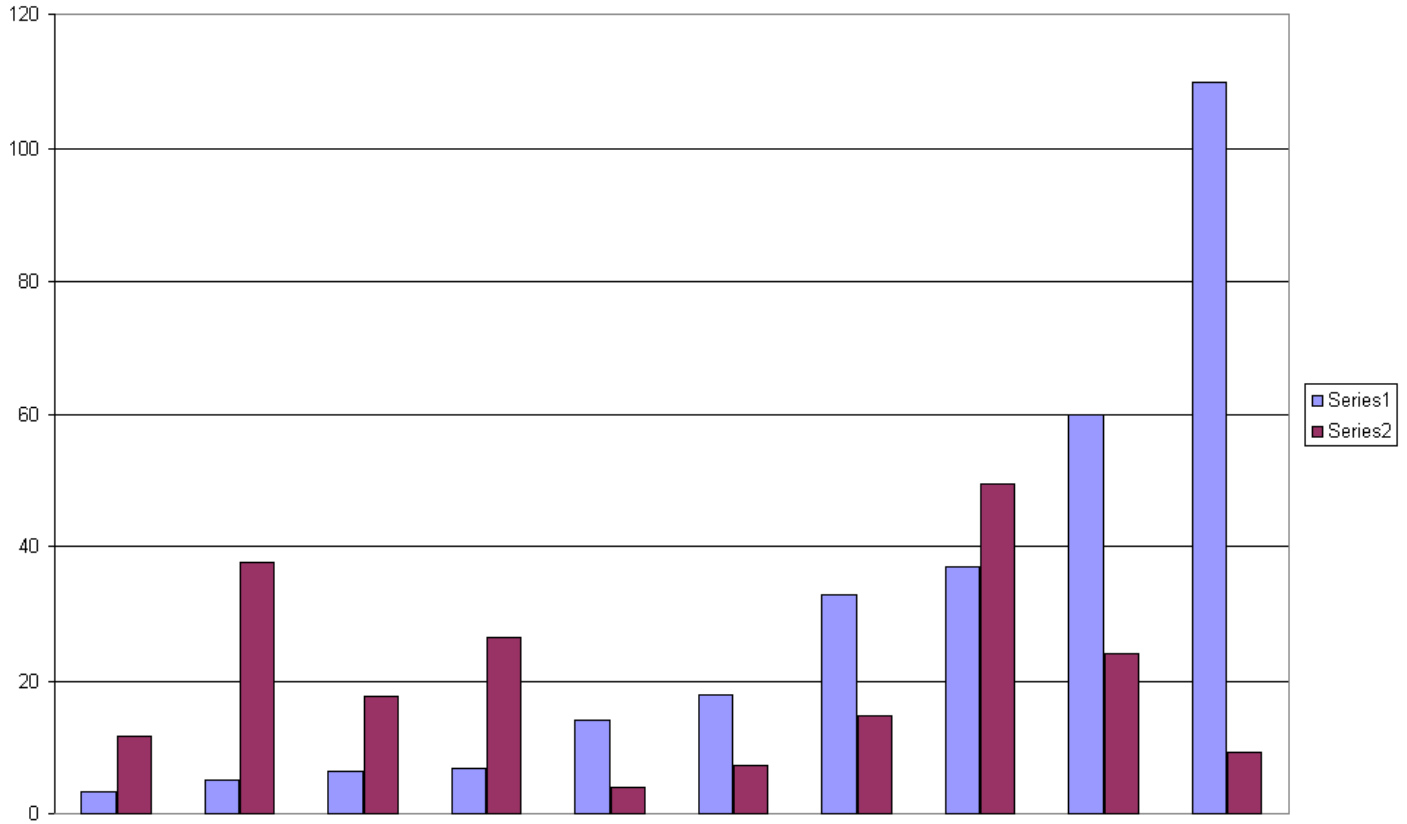
Change in performance



Protocol

- Protocol includes a step to purge the regulators,
- This is an important step
- a) Attach regulator to cylinder and tighten connection.
- b) Turn regulator pressure control off (anti-clockwise)
- c) Ensure regulator shut-off valve is closed.
- d) Quickly open and close cylinder valve to pressurise regulator.
- e) Set regulator pressure control to a few bar (15-30psi).
- f) Open regulator shut-off valve to purge then close shut-off valve.
- g) Quickly open and close cylinder valve to pressurise regulator.

- Repeat steps f) and g) three times.

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Uncertainty from the PT scheme

- Check results against your uncertainty budgets
  - Too small – look for errors or unforeseen sources of uncertainty
  - Too large – review uncertainty budget, check which components are not relevant to pt scheme measurements

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Future

- Particulates/ Weighing
  - Shim
  - Rinse solution
- Stack simulator

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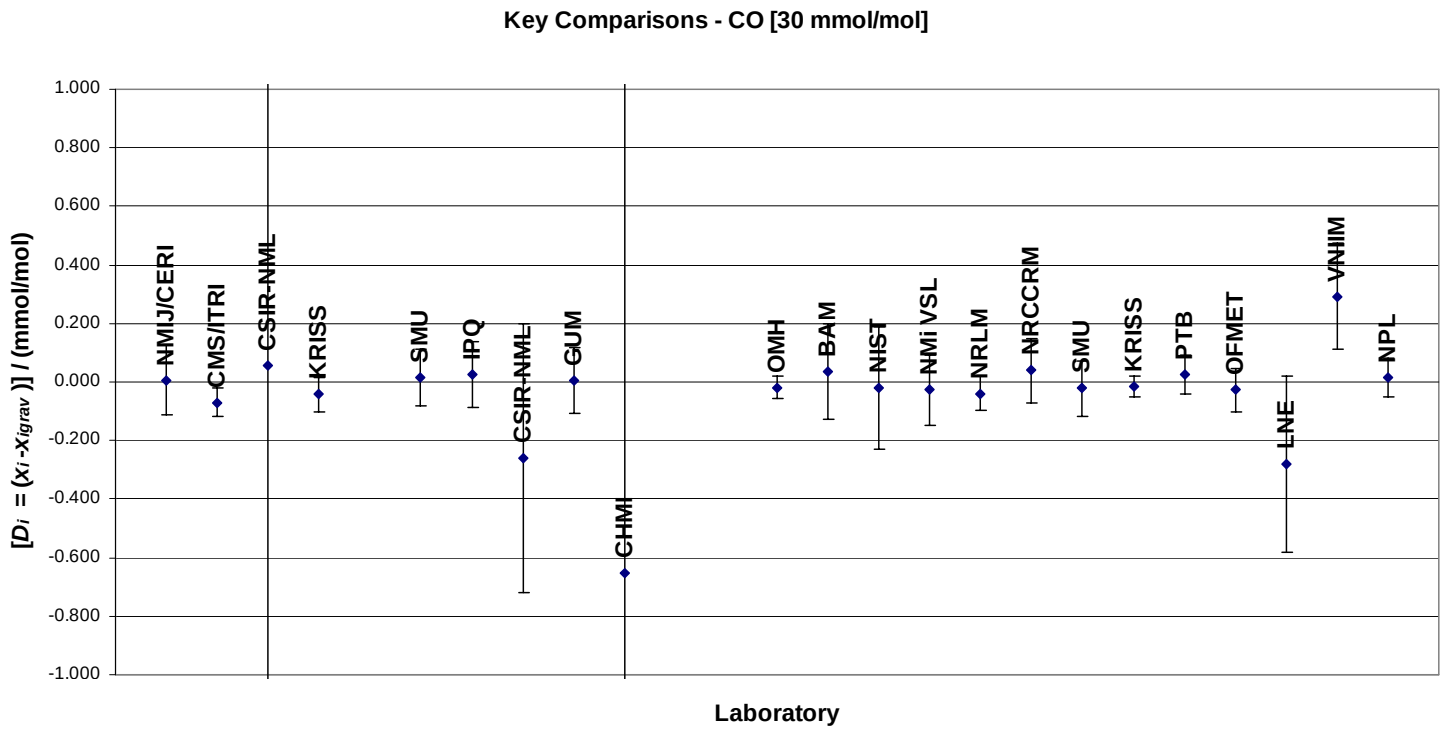
Key Comparisons – CO Results