Setting standards in analytical science

ESTABLISHING TRACEABILITY FOR CONSENSUS MEANS

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Traceability

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Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having state uncertainties

Traceability Requirements of ISO17025

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- An important requirement of quality standards such as ISO 17025 and ISO Guide 34 is that test results or values assigned to reference materials should be traceable, preferably to national or international standards.
- Time and cost constraints often preclude full characterisation of matrix reference materials by primary methods and inter-laboratory studies are widely used to establish consensus mean values for their certification.

Previously…….

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- It has argued that the traceability of matrix RMs can be established through
  - Primary or reference measurements traceable to the SI
  - Consensus values based on methods of known bias
    - Although bias may not have been fully evaluated for each method, where results from the different methods agree it can be concluded that bias is absent
  - Traceability of reported participant results
    - Provided the consensus agrees with at least one independent measure of the assigned value, it can be used to set the traceable assigned value.

  [King et al, 2003]

Establishing Traceability in Practice

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- LGC has previously proposed an approach for inter-laboratory data which involves providing an accurately prepared and verified instrument calibration solution to each participant laboratory in addition to the candidate reference material.
- However, just because a laboratory can successfully analyse a solution does not mean it can competently analyse a matrix material.

- Here we examine this further…….

Approaches Evaluated

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- All laboratories with data corrected on basis of result from a QC sample
- Laboratories which met required criteria for QC sample
- Laboratories with ISO17025 accreditation

- Compared assigned values against data from all laboratories

Anions in Drinking Water

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- The determination of analytes in aqueous matrices (river, rain and drinking water) is
  - relatively simple
  - extensive sample preparation prior to the instrumental measurement step is not usually required.
  - Often the sample may be analysed by direct introduction to the instrument, with minimal preliminary preparation.
- observed between-laboratory variation is determined
  - by the variations in the instrumental measurement procedures
  - and by variations in the individual ***instrument calibration standards*** used by different laboratories.

Analytes in Food Matrices

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- The determination of analytes in more ‘complex’ matrices, such as sediments, sludges, and food-type matrices:
  - usually comprises a sequence of steps (e.g. digestion, extraction, and clean-up)
  - followed by instrumental measurement.
- In a complex measurement process such as this, the entire process must be validated in each laboratory, so that each laboratory can demonstrate that it is producing reliable results.

Examples……

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- Anions in drinking waters
  - QC – gravimetrically prepared solutions
- Metals (Sn, Pb, Cd) in a food matrix
  - QC – gravimetrically prepared solutions
- SO_2 in potato powder
  - QC – units from previous batch of material

Tin – QC results

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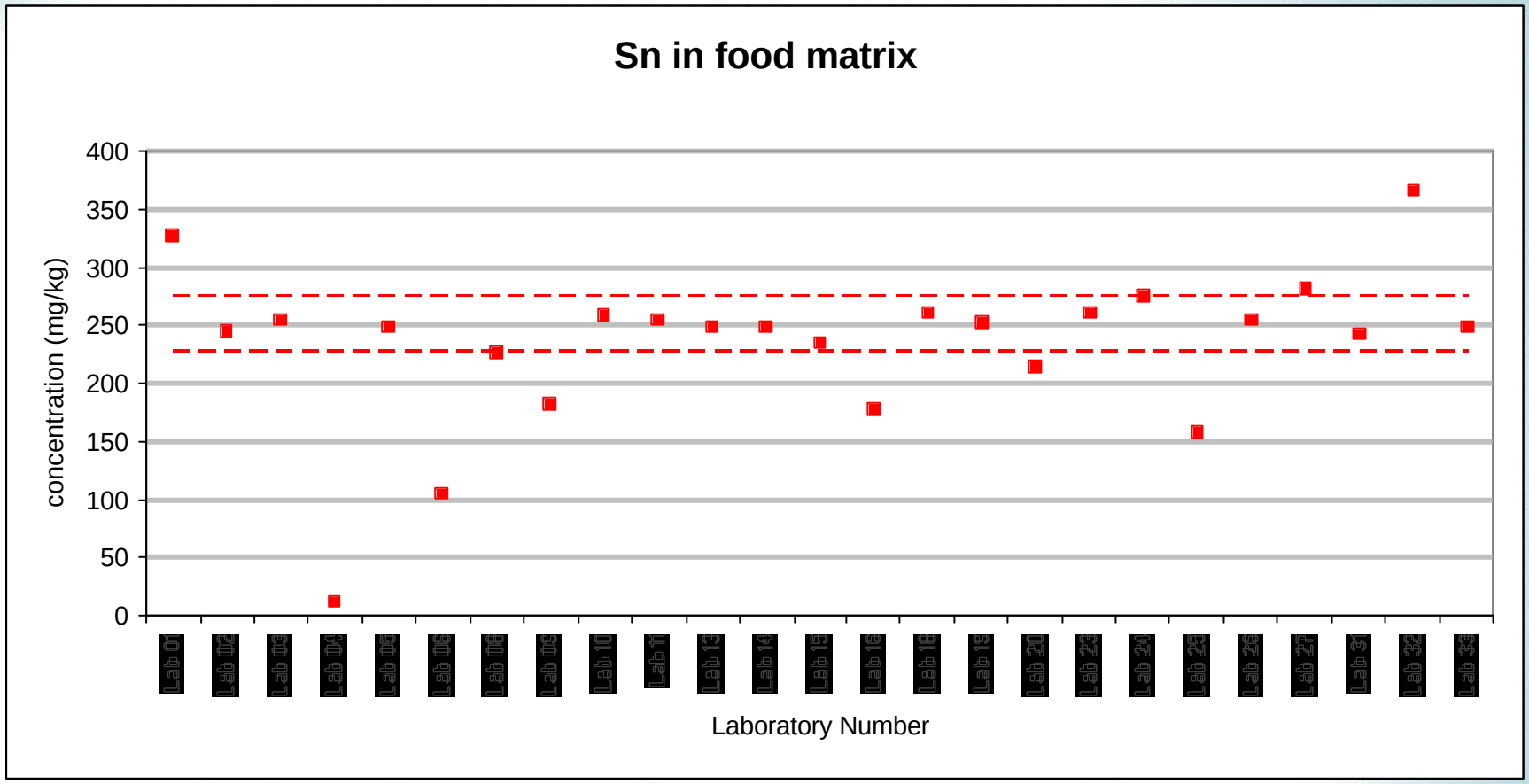

Gravimetrically prepared QC solution 250.5 mg/kg Sn

Tin – reported results

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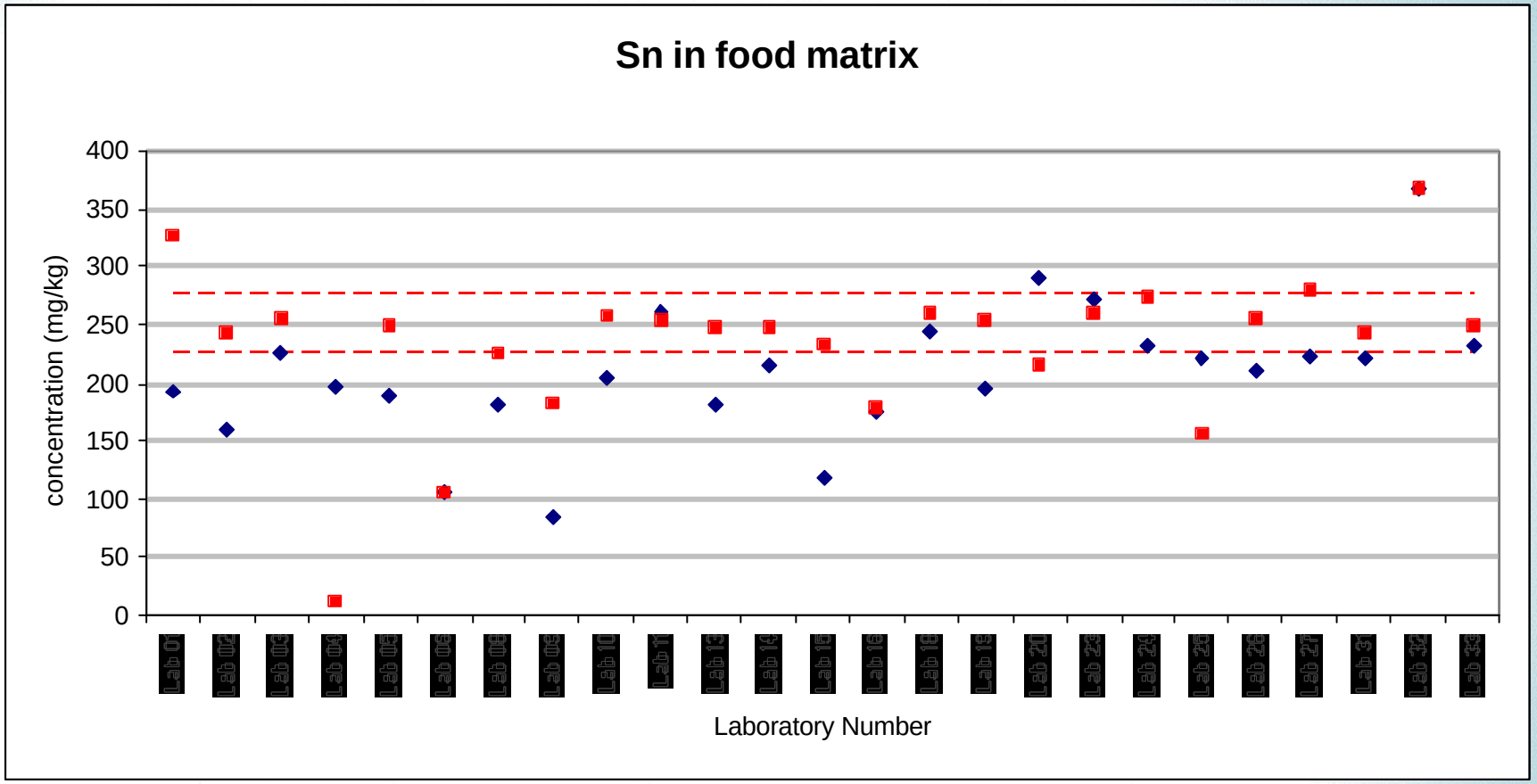

Correction for QC value

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$$CRM_{corrected} = CRM_{reported} \times \frac{QC_{expected}}{QC_{reported}}$$

Applying QC correction

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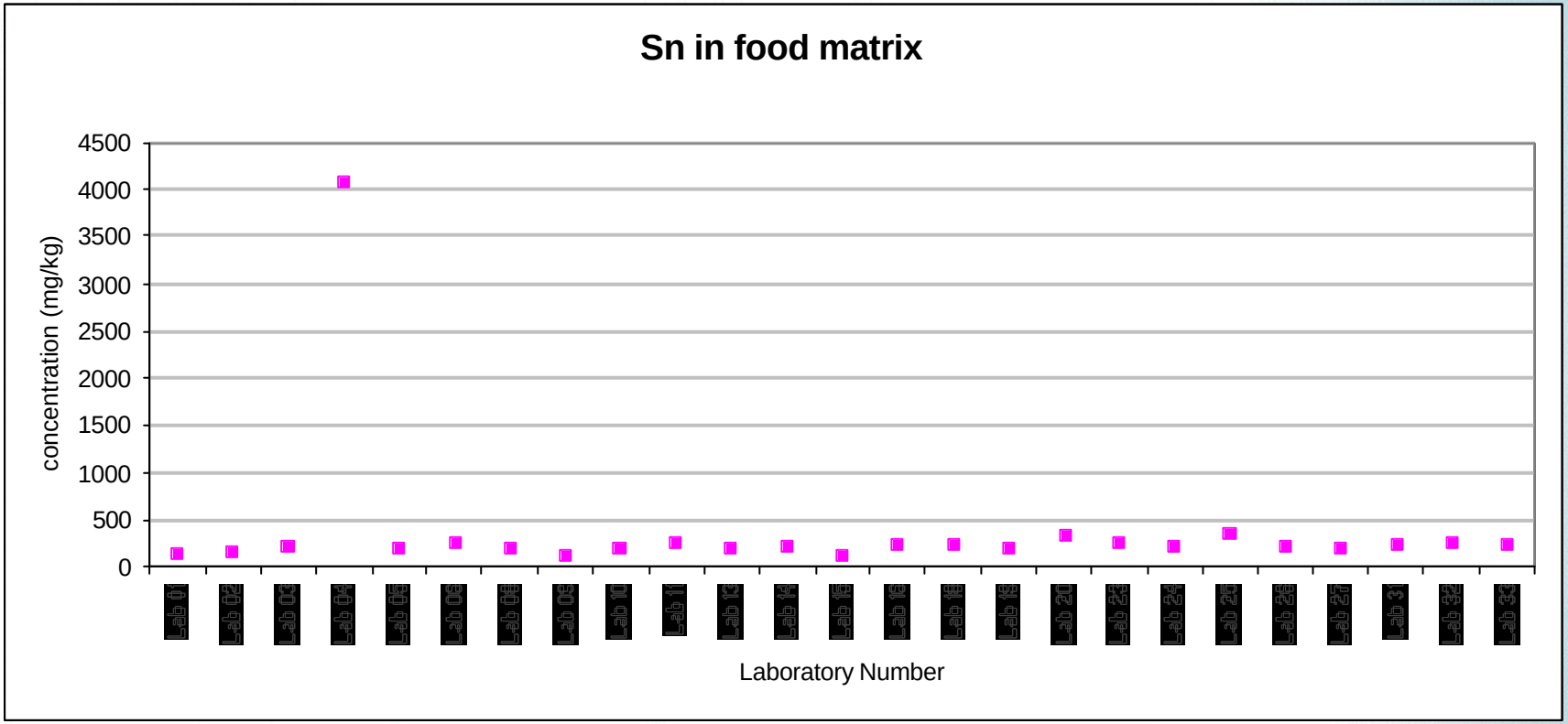
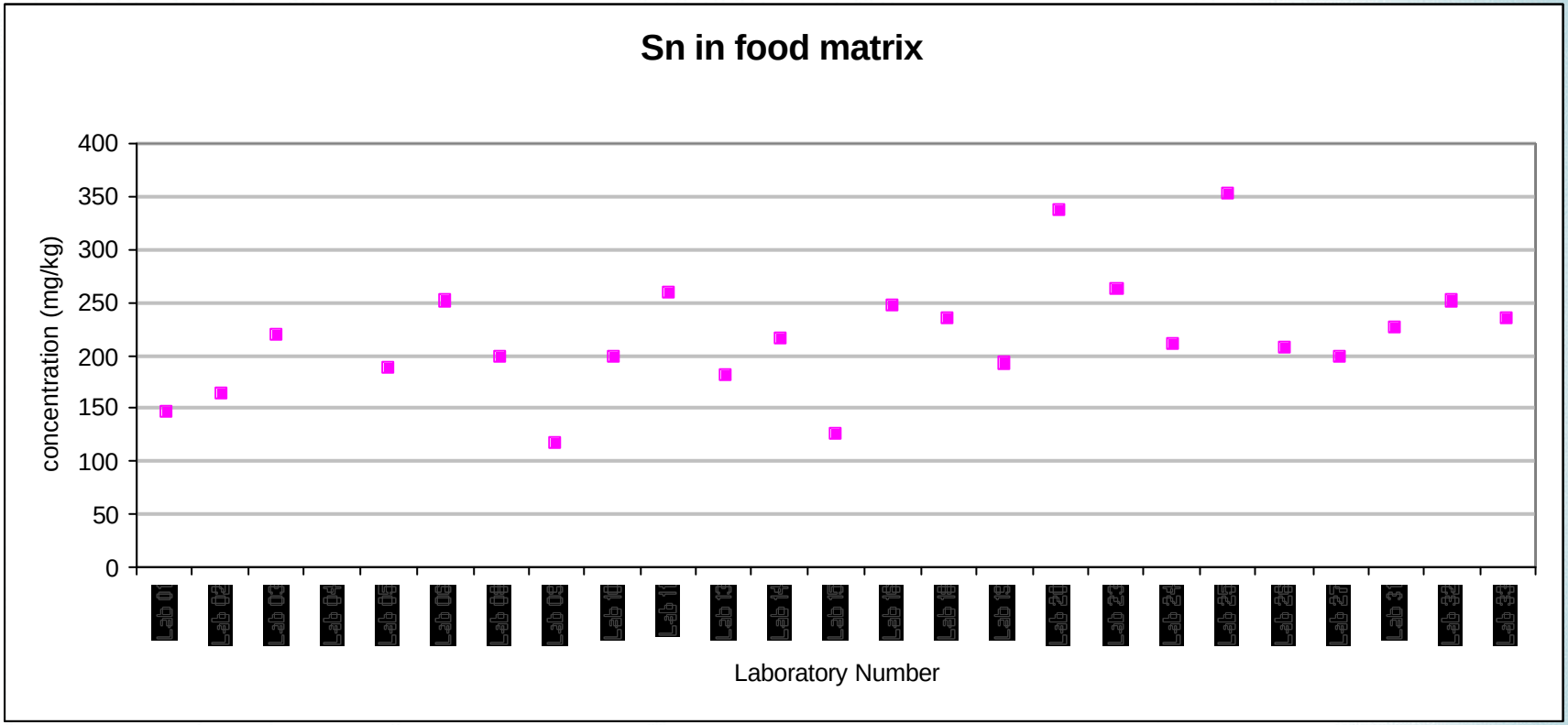


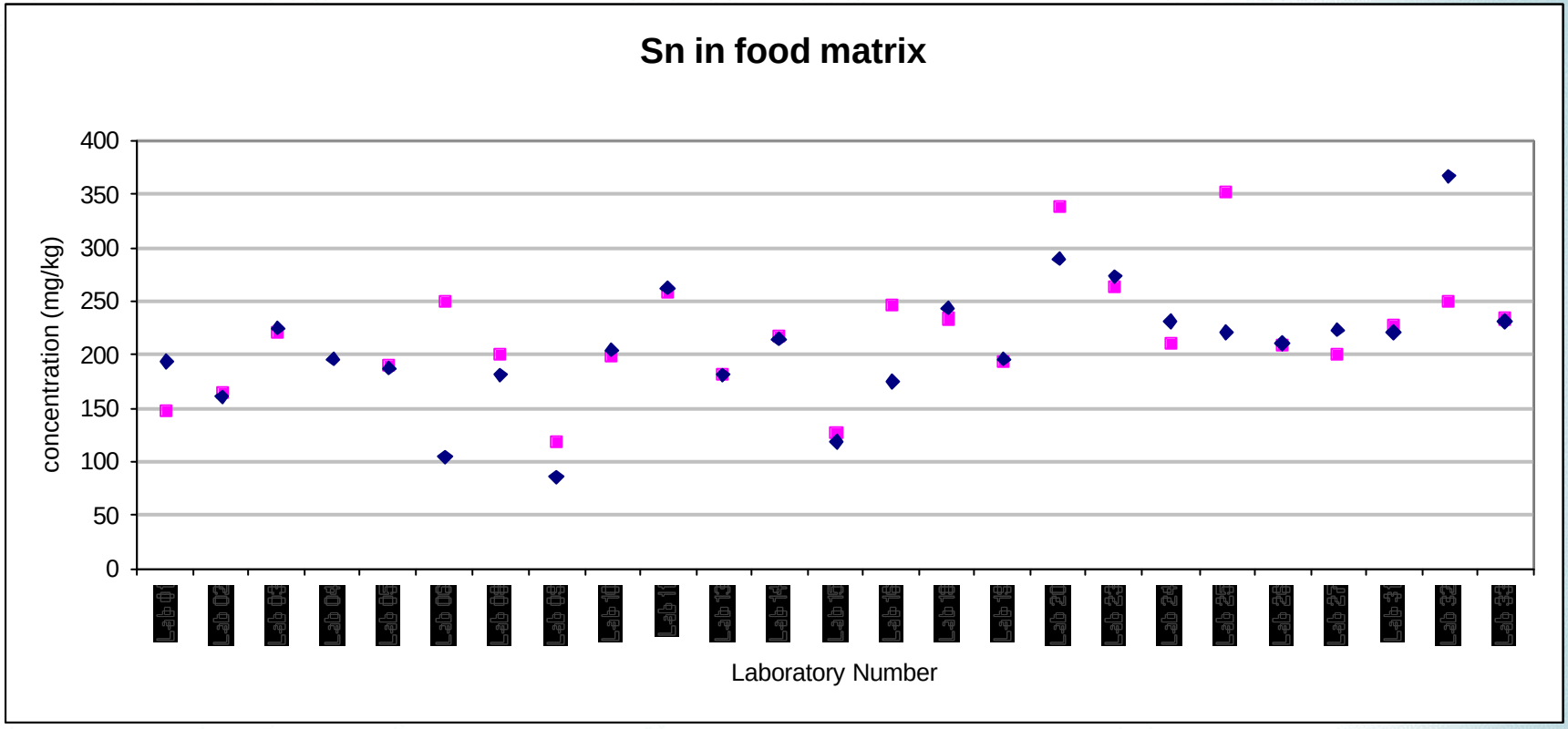
Applying QC correction

Setting standards in analytical science



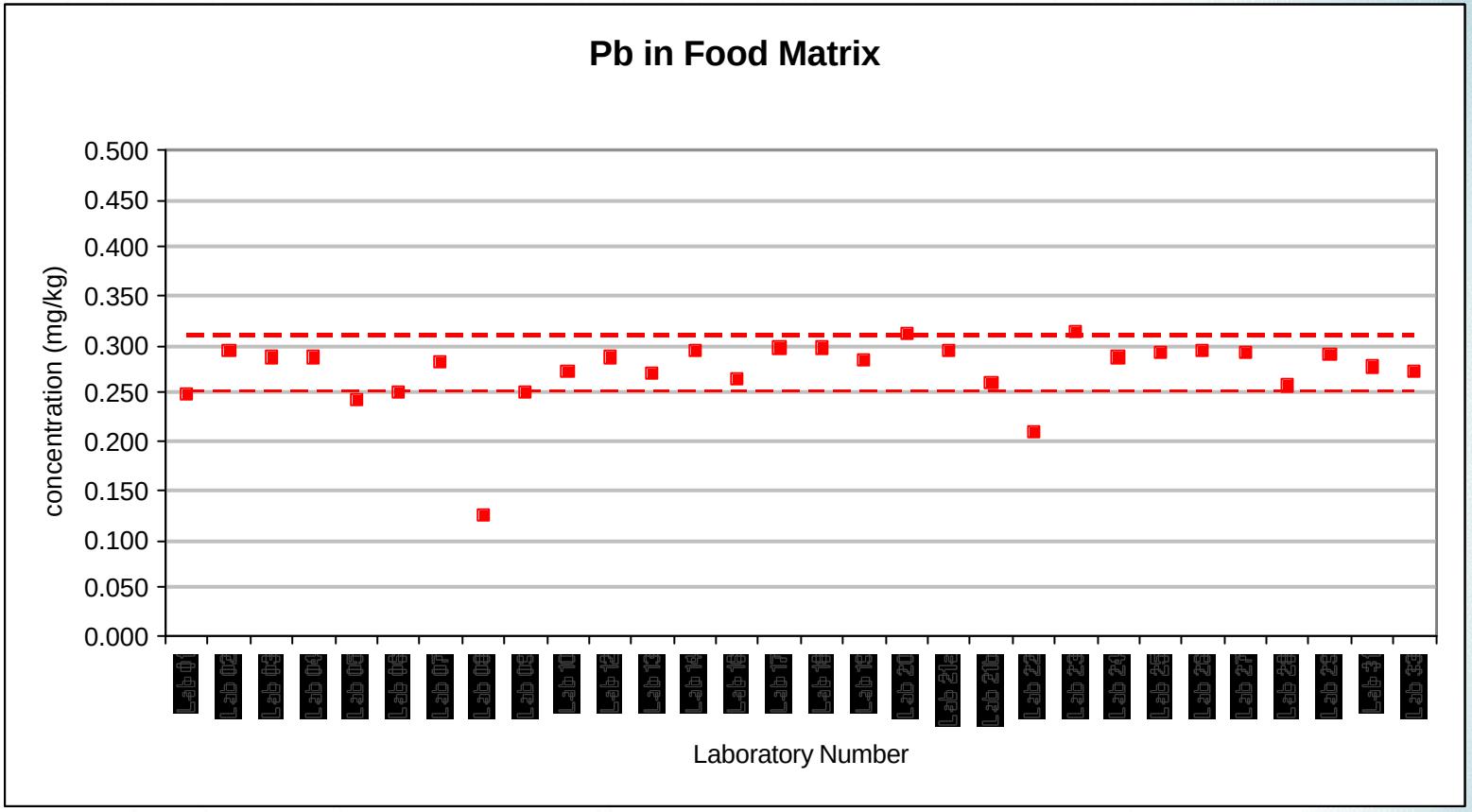
Corrected vs reported results

Setting standards in analytical science



Lead – QC results

Setting standards in analytical science



Gravimetrically prepared QC solution 0.280 mg/kg Pb

Lead – reported results

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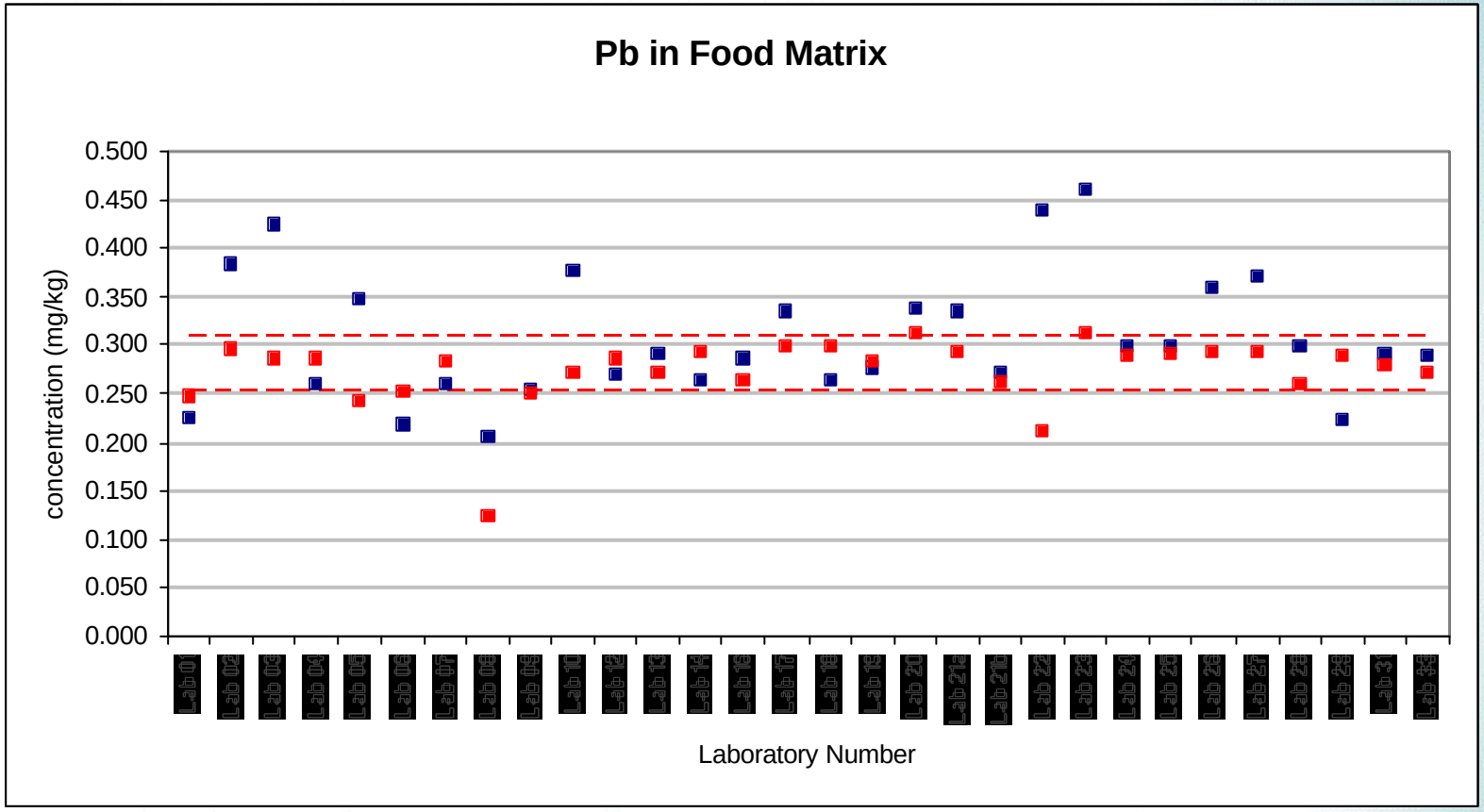
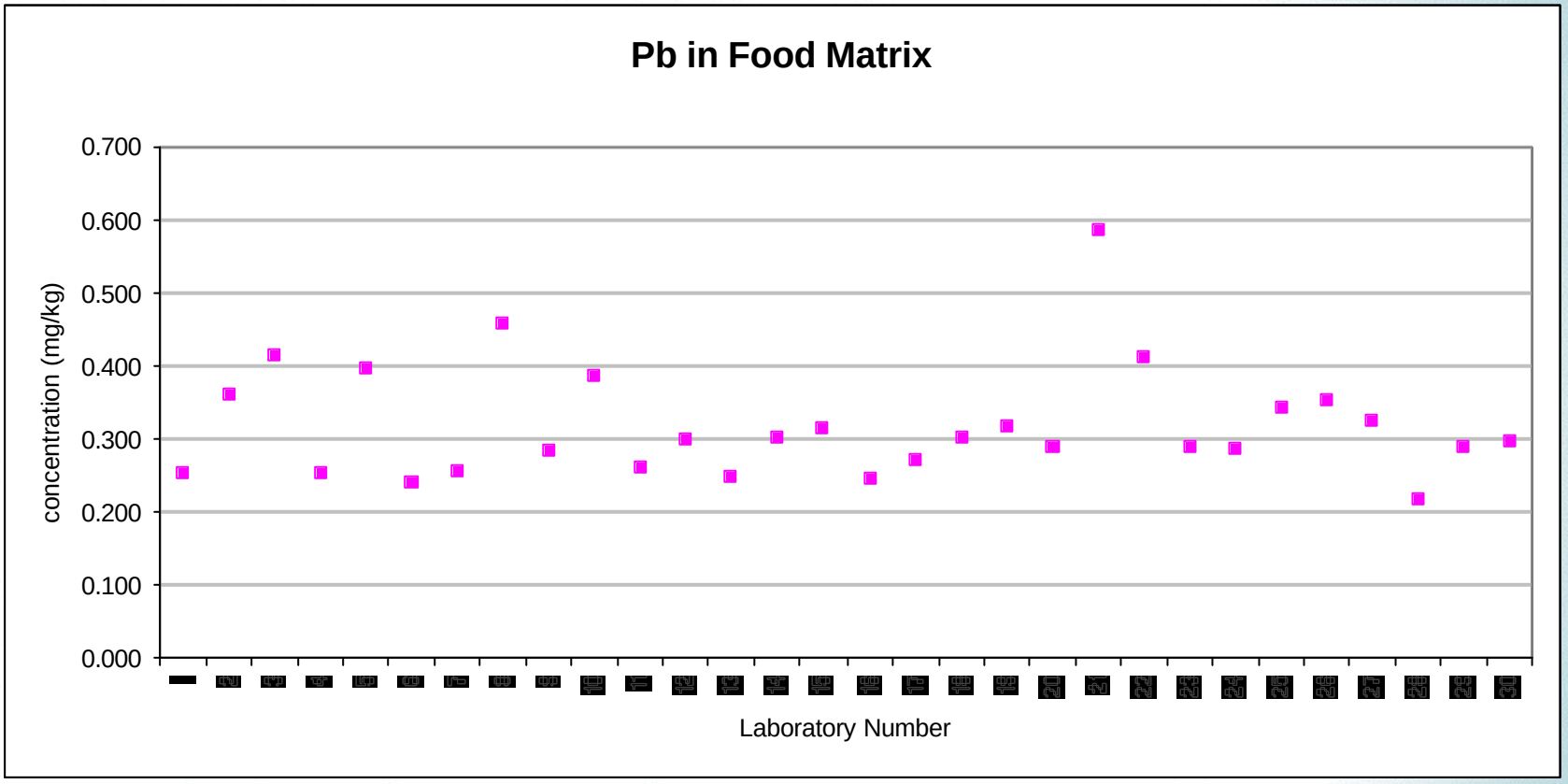


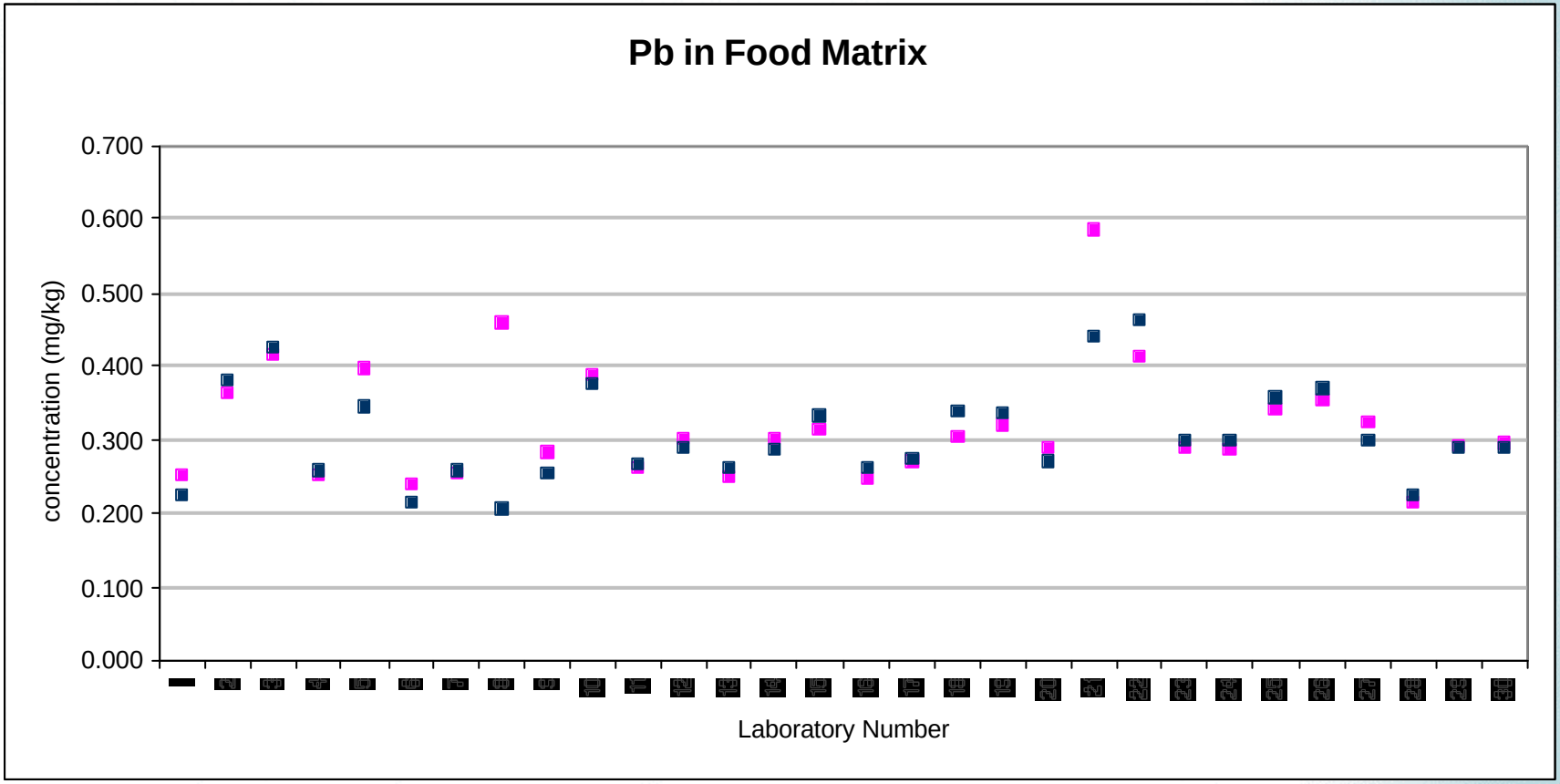
Applying QC Correction

Setting standards in analytical science



Corrected vs reported results

Setting standards in analytical science



Cadmium – QC results

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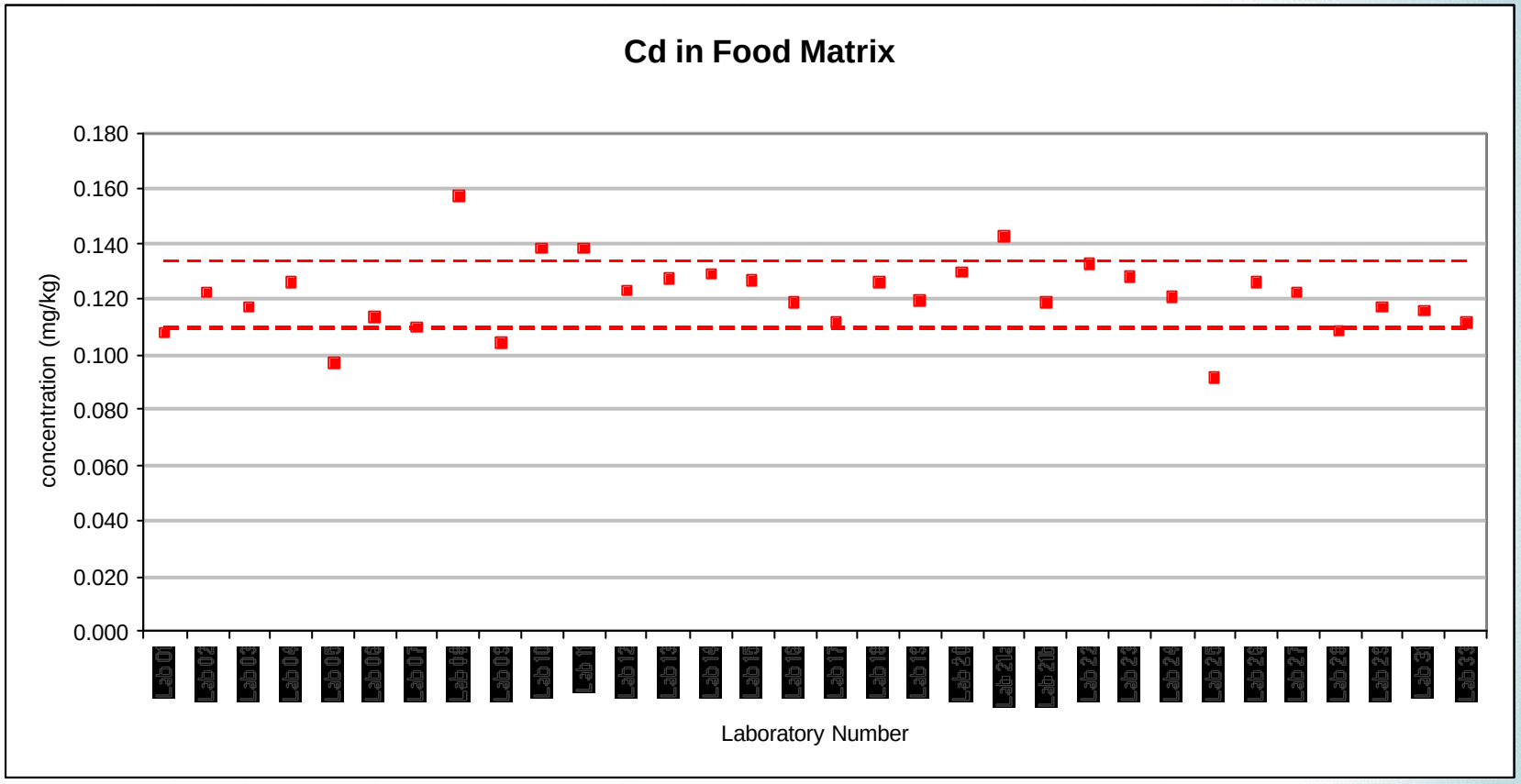

Gravimetrically prepared QC solution 0.1212 mg/kg Cd

Cadmium – reported results

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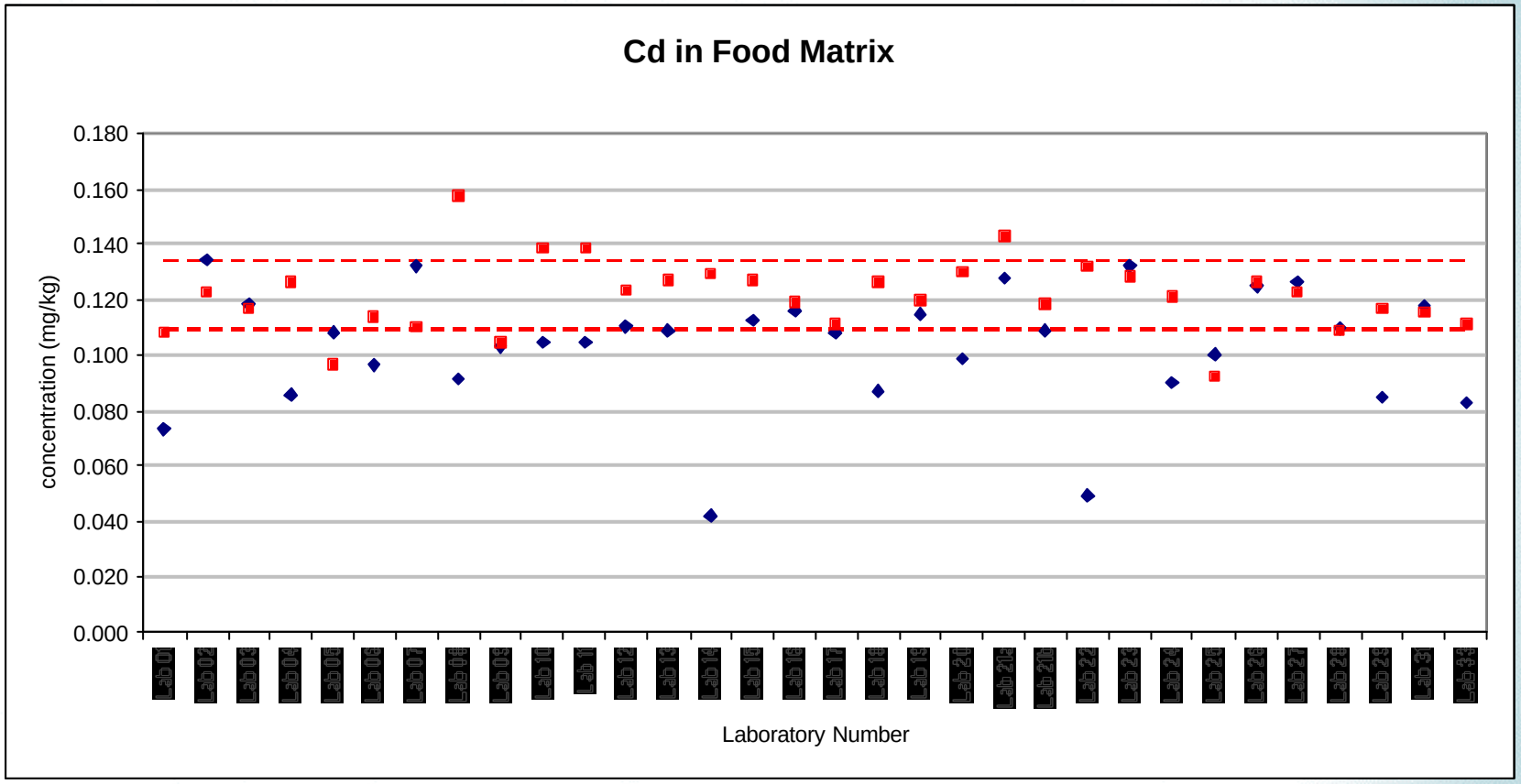

Applying QC Correction

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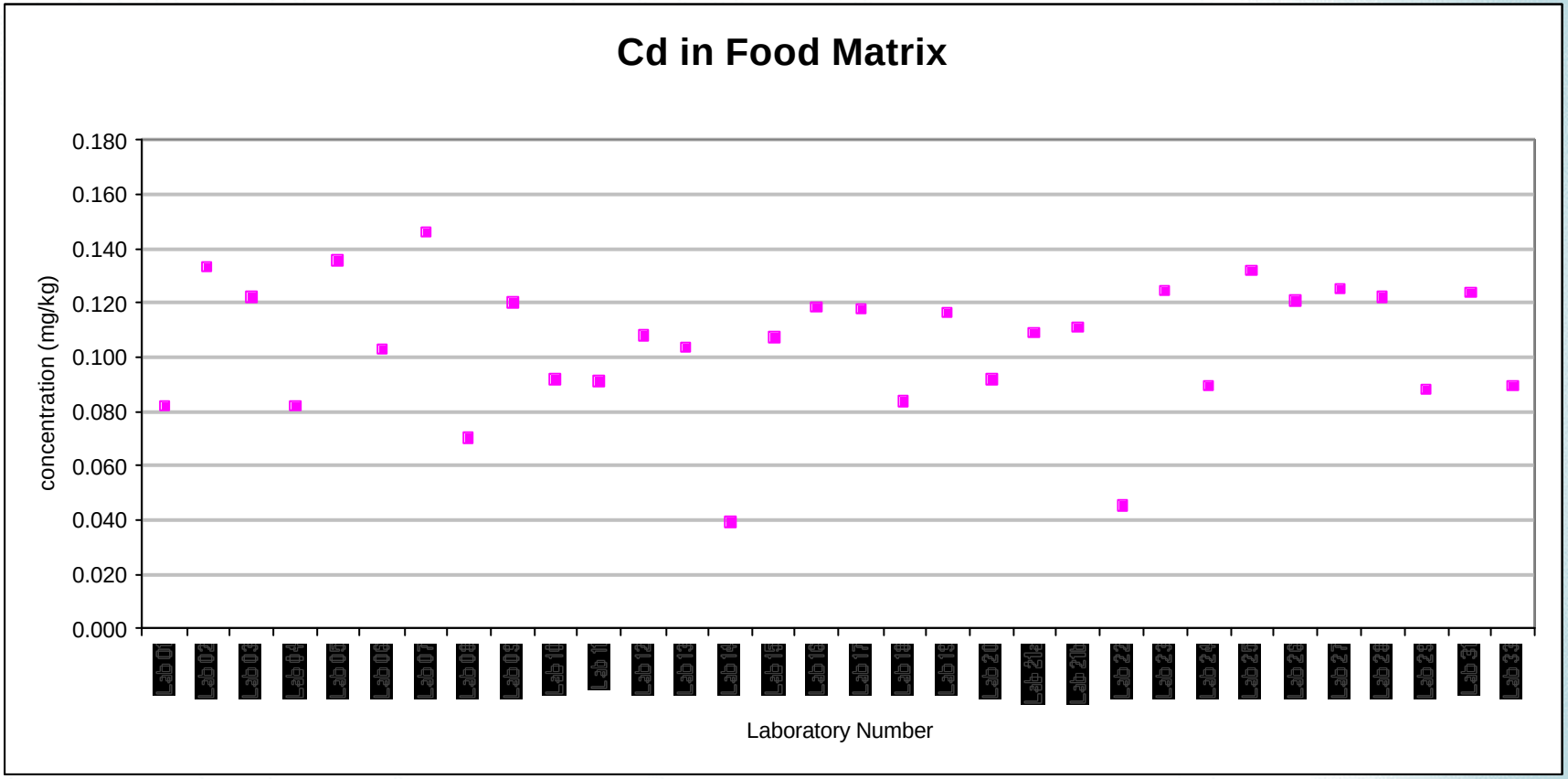
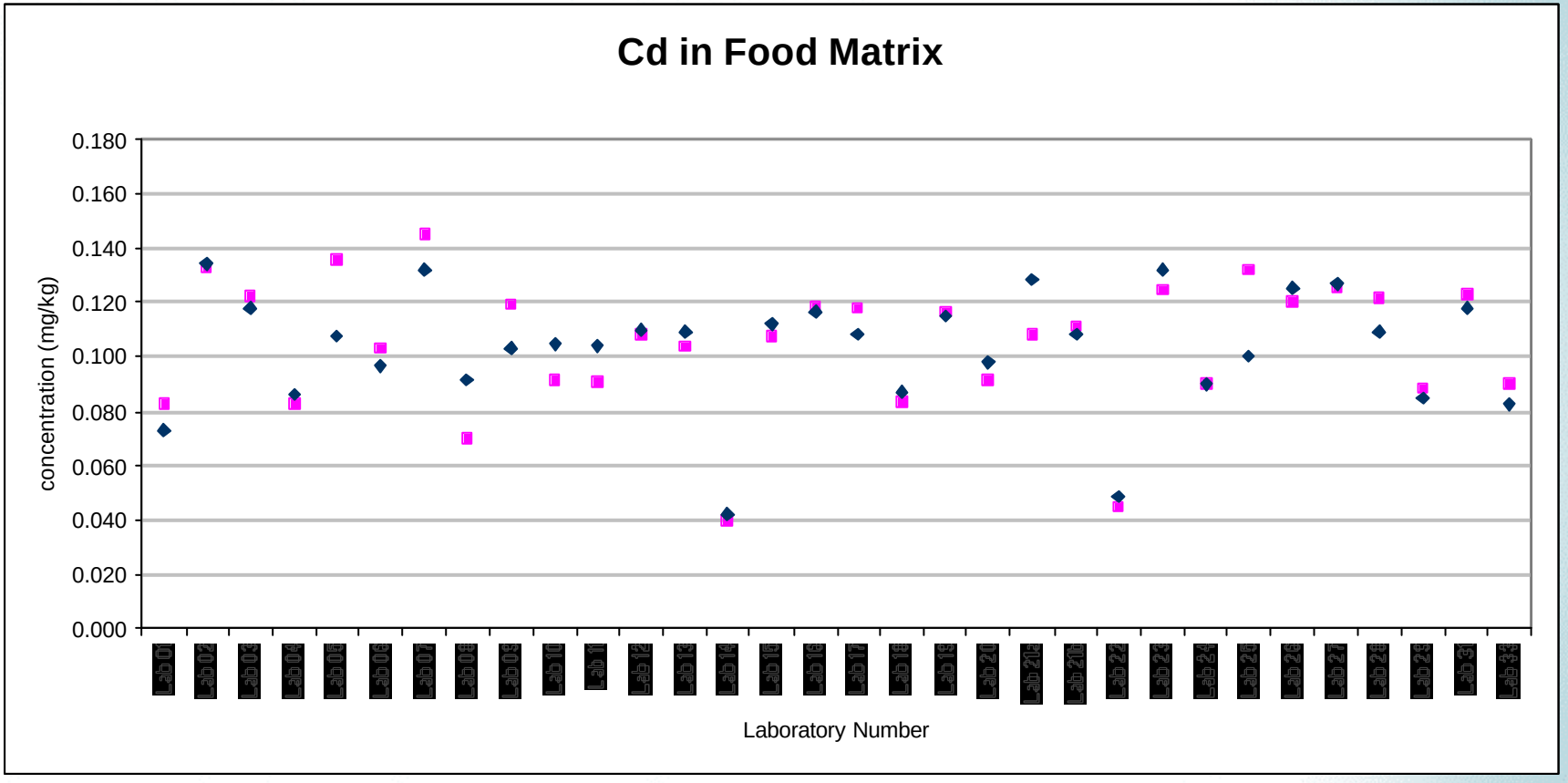


Corrected vs reported results

Setting standards in analytical science



SO_2 in Potato Powder

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- In this study, participants were provide with a unit of material from the previous batch of the reference material as the QC.

- The QC and the candidate material were thus the same matrix and analysis of the QC required the same process stages as the candidate material.

QC results

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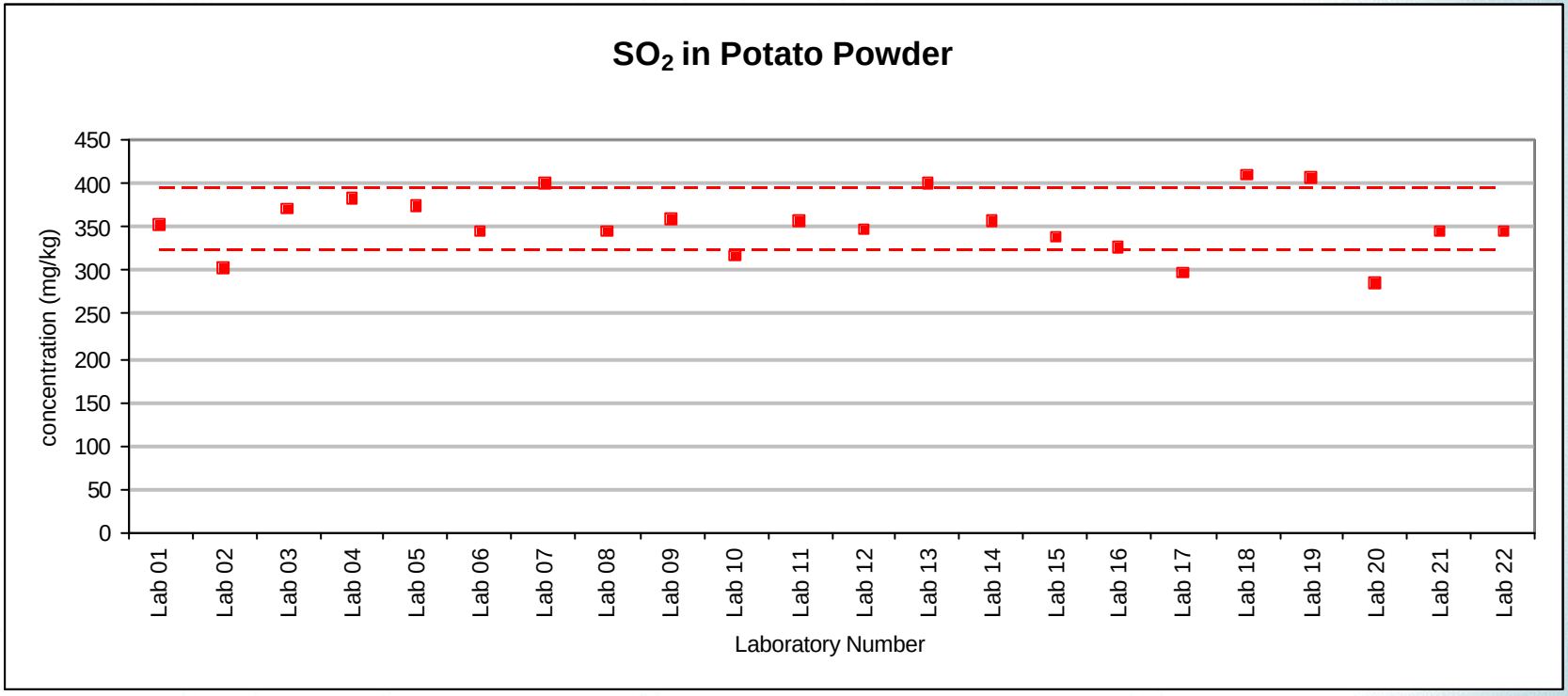
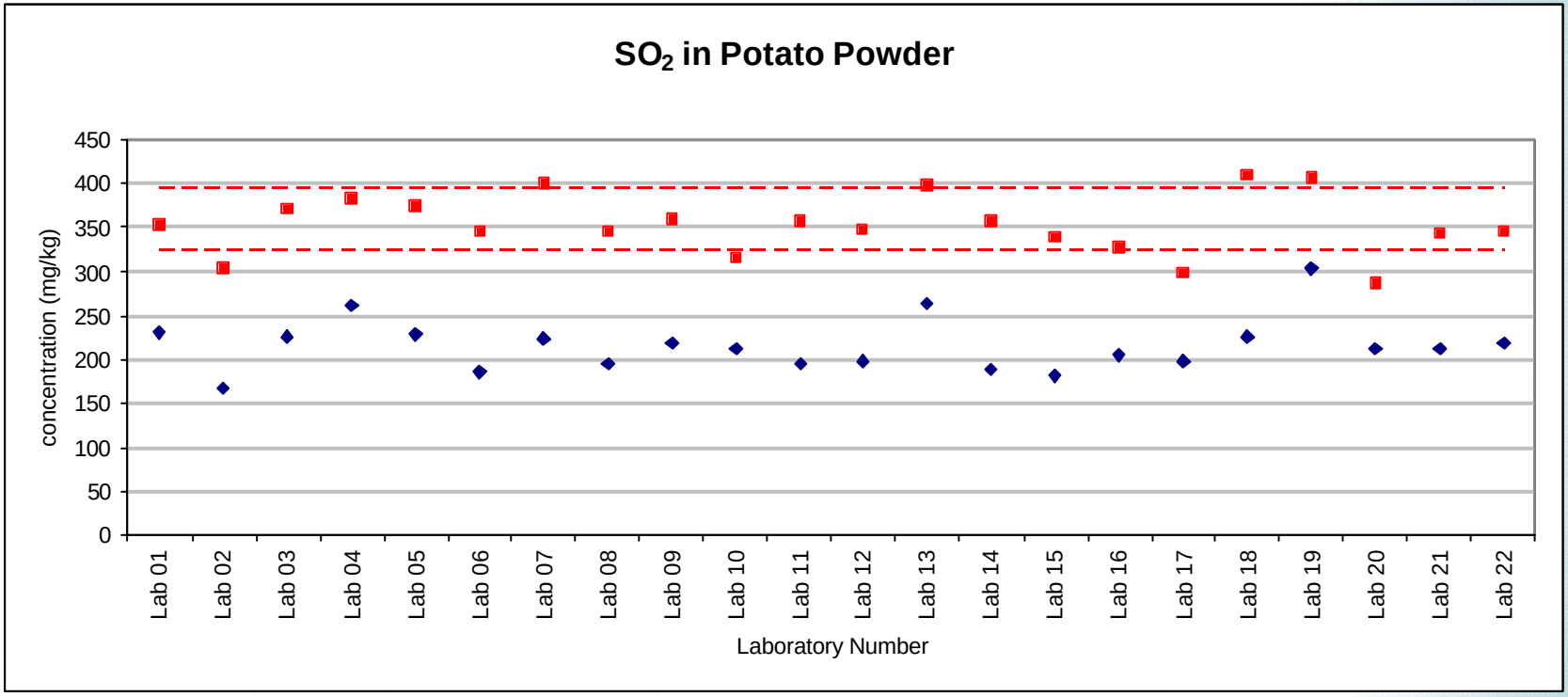


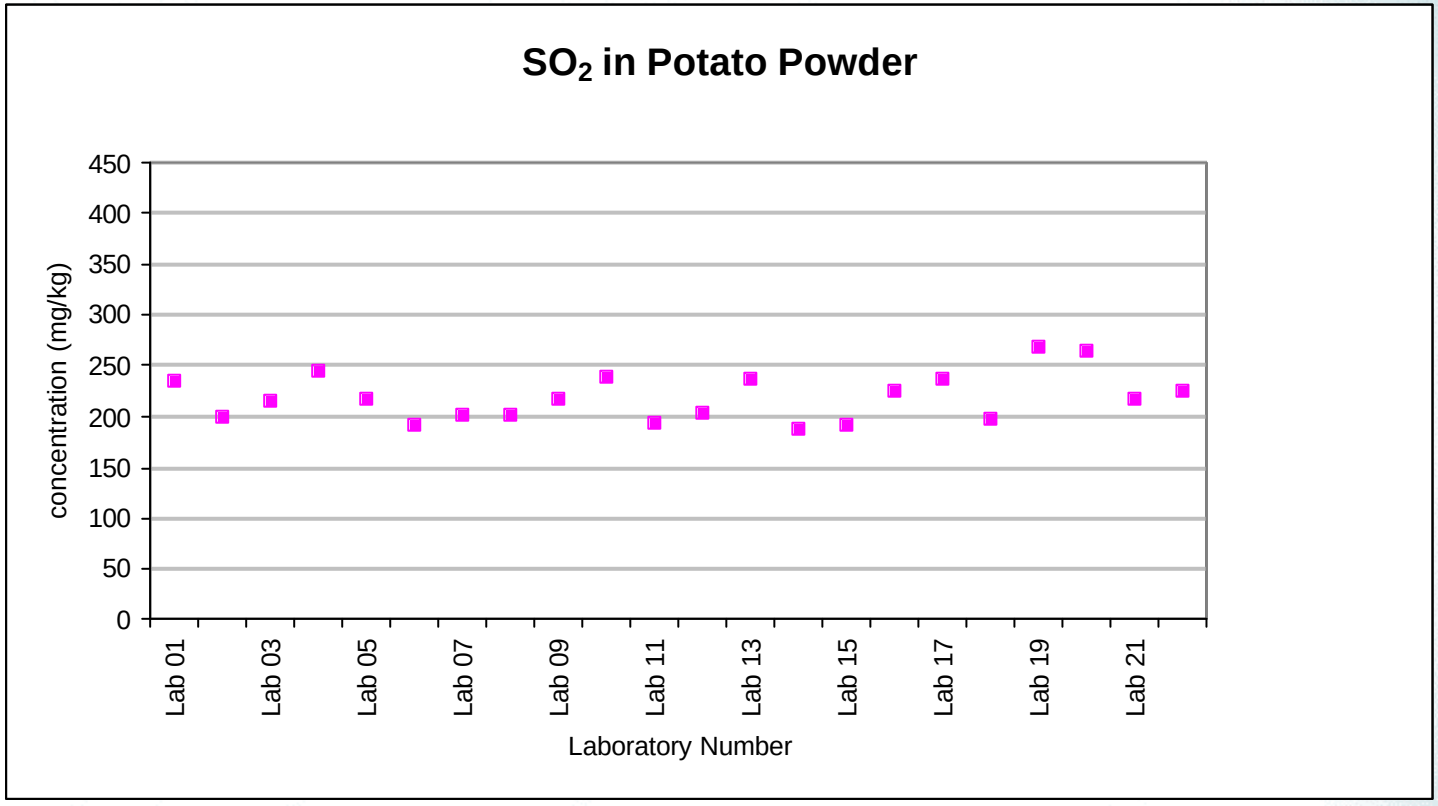
Reported results

Setting standards in analytical science



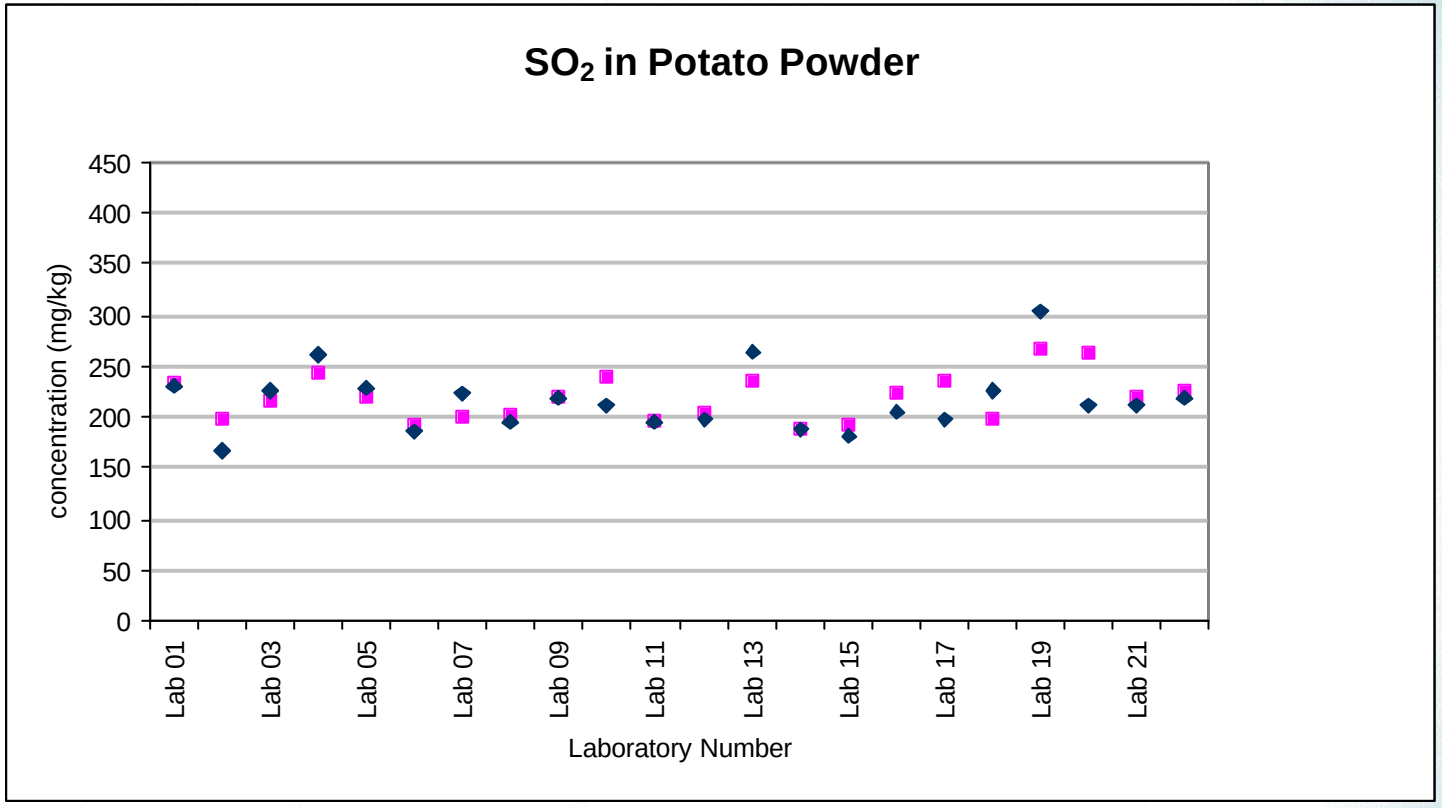
Applying QC correction

Setting standards in analytical science



Corrected vs reported results

Setting standards in analytical science



Uncertainty of corrected value

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- Must take into account the uncertainties of the consensus value and the QC material

$$u_{corrected} = \sqrt{u_{consensus}^2 + u_{QC}^2 + ...}$$

- For the potato powder QC
  u_{QC}= 10%

$$u_{batch2} > u_{batch1}$$

Comparing Other Approaches

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- All laboratories with data corrected on basis of result from a QC sample
- All laboratories
- Laboratories which met required criteria for QC sample
- Laboratories with ISO17025 accreditation

Normal & Robust Statistics

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- Normal Statistics
  - all labs
  - outliers removed
  - all accredited labs
  - all accredited labs with outliers removed
  - all non accredited labs
  - non accredited labs with outliers removed
  - data corrected for QC, all labs
  - data corrected for QC, with outliers removed
- Robust Median/MADe
  - all labs
  - accredited labs only
  - non accredited labs only
  - data corrected for QC, all labs
- Other robust methods applied
  - H15 estimator
  - Mixture model median

Effect of different processing approaches

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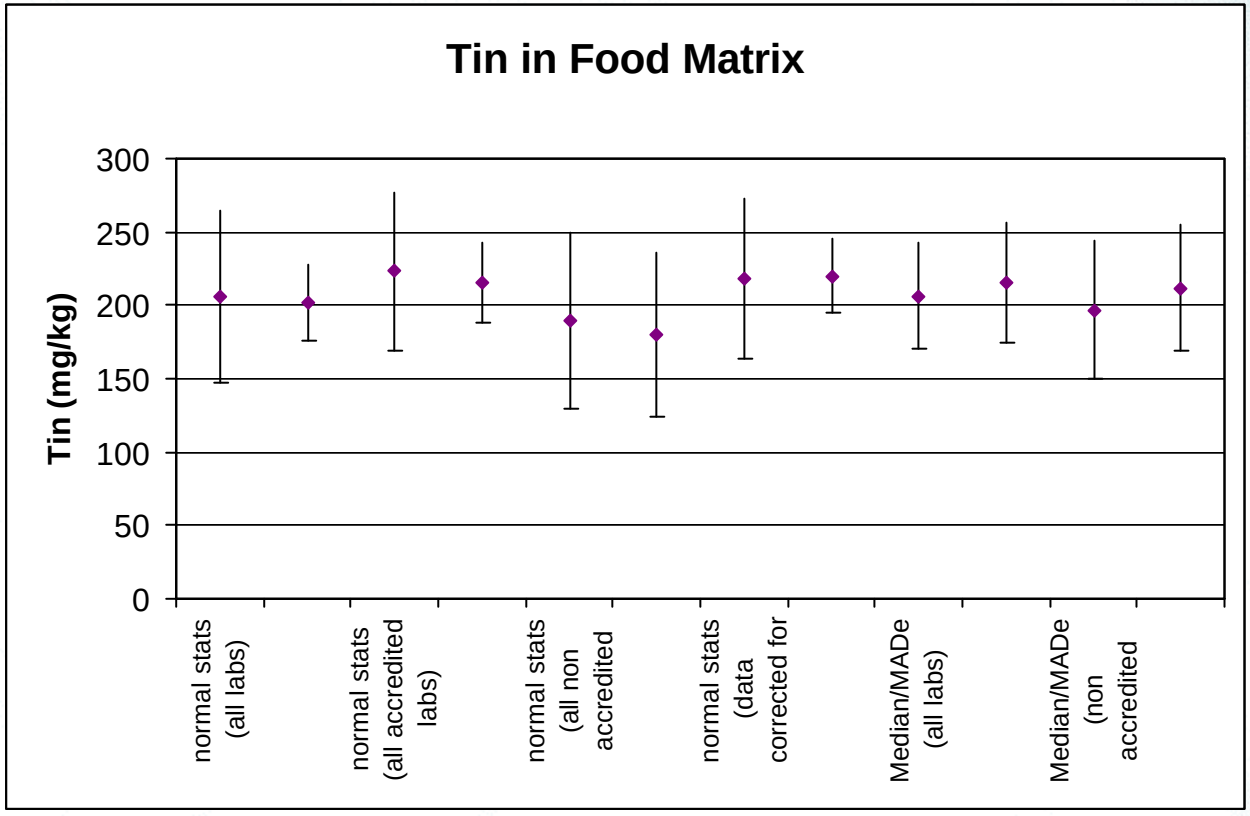

Considerations (1)

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- Does this give traceability
- How to select QC material
- Is QC material itself traceable
  - E.g. SO_2 in potato powder, QC was sample from previous batch, itself characterised by an inter-laboratory study.
  - Gravimetrically prepared solution e.g. anions in water
  - CRM from NMI supported with through a CCQM key comparison study
- Additional study in progress characterising a matrix soil material, using a matrix soil as QC.

Conclusions

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- Is (metrological) traceability of consensus means achievable?
  - Possible – where the following conditions are met
    - Fully traceable QC material
    - QC material directly applicable to test sample/matrix
  - Questionable when:
    - Partially traceable QC material
    - QC material not directly applicable to test sample/matrix
    - ISO17025 laboratories
  - Not when
    - Partially traceable QC material
    - No appropriate QC material available