Where we are now on Quality Assurance and where do we need to be? Some thoughts on fit for intended purpose analysis with water test kits

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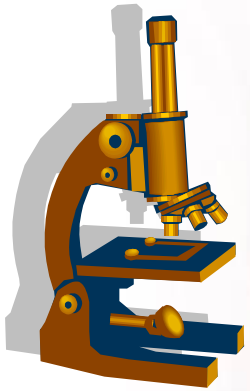
Where we are now on Quality Assurance and where do we need to be? Some thoughts on fit for intended purpose analysis with water test kits

1. Introduction and background
2. Sampling issues
3. Analysis issues
4. QA/QC issues
5. Regulatory limits
6. Conclusions

1) Introduction and background



Contents of BS 1472:2008 Guide to on-site test methods for the analysis of waters (120 pages)

Progress to date on BS 1427 Guide to on-site test methods for the analysis of waters

- **Last few final comments from a restricted second consultation that closed on 31st Oct 2008 to be reviewed**
- **Due for publication in Dec 2008**
- **A one day RSC/SCI seminar in London being arranged to promote it in Feb 2009**

Types of waters for which the tests are intended (lightly polluted waters)

a) boiler waters;
b) cooling waters;
c) waters from hot water systems;
d) waters from air conditioning systems;
e) waters from industrial air washing systems;
f) potable waters;
g) ground waters;
h) surface waters;
i) process waters; and
j) swimming pool waters.

More polluted waters

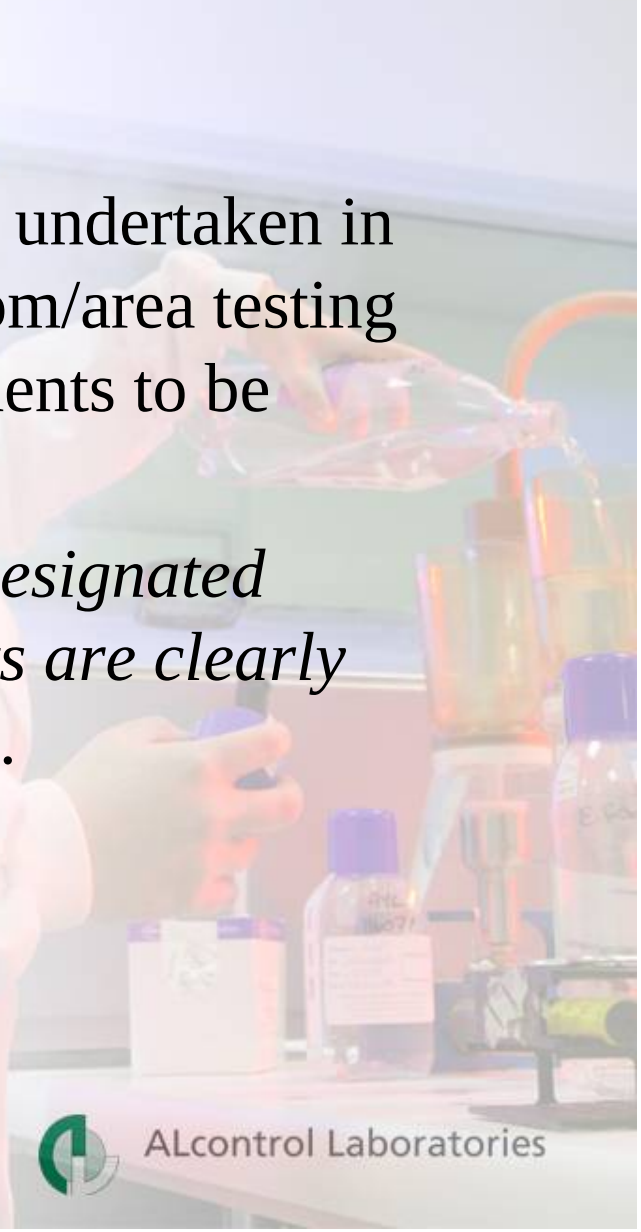
- All revelant water matrices need to be validated. For more polluted waters, the user needs to ascertain the worst case likely interference effects and the effects of suspended or colloidal material present
- Spike recovery tests will only indicate method sensitivity changes. They will not highlight interference effects caused by turbidity and colour
- Turbidity and colour have a proportionally larger effect at lower analyte concentrations than at high concentrations

Definitions (1)

on-site tests

quantitative chemical and physical tests undertaken in situ on a site, or within a designated room/area testing facility, to enable water quality assessments to be undertaken

NOTE Some on-site tests do require a designated room/area testing facility and these tests are clearly indicated in this standard (See Annex I).



Definitions (2)

designated room/area testing facility

basic laboratory facilities in a designated room (or a designated secure area in a room)

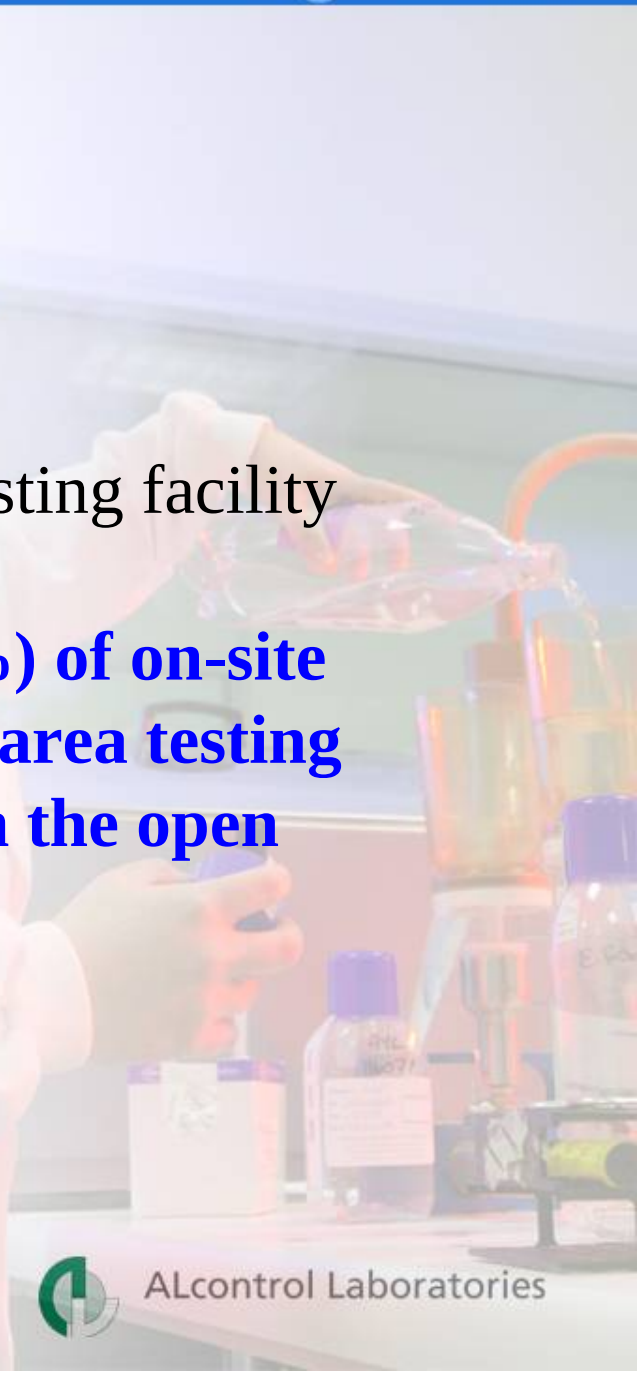
NOTE 1 This could include provision of electricity, fixed bench facilities, water supply and suitable drainage; analytical balance, heating block, fume extraction etc. Other uses of the room or area have to be controlled so as not to interfere in any way with the analysis. This should include controlled access and restricted activities compatible with use as a test area. For some tests this could include dedicated space in a designated vehicle or caravan.

Definitions (3)

designated test room/area test

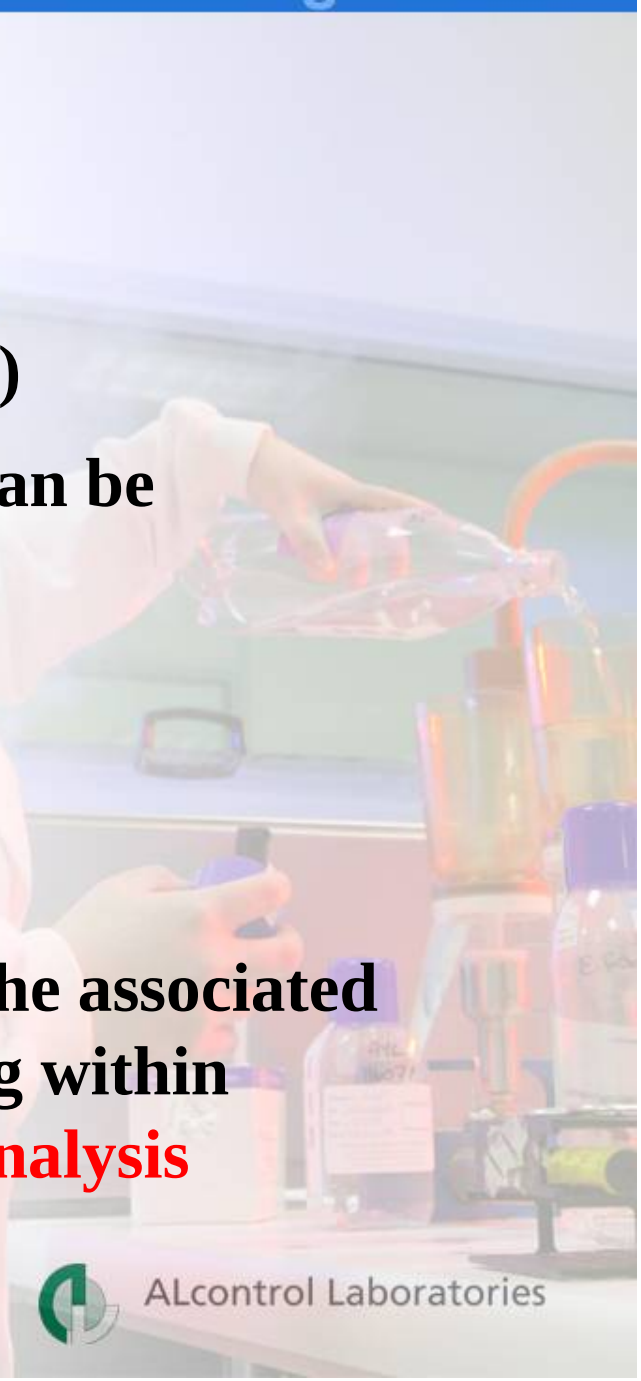
test that requires a designated room/area testing facility

It would appear that the majority (~90%) of on-site tests are carried out in designated room/area testing facilities rather than being carried out in the open



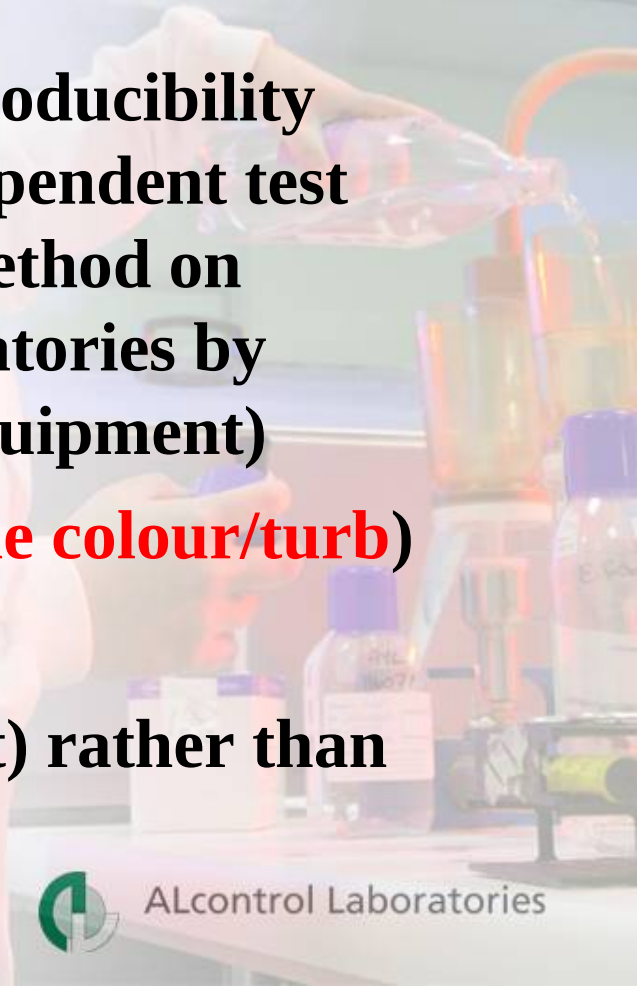
Definitions (4)

- **precision**
- **trueness (the systematic error or bias)**
- **uncertainty (No part of uncertainty can be corrected for.)**
- **accuracy**
- **method validation**
- **system suitability checks (SSC).**
  SSCs are simple tests to ensure that the associated test-kit instrumentation is functioning within specified limits before commencing analysis



Definitions (5)

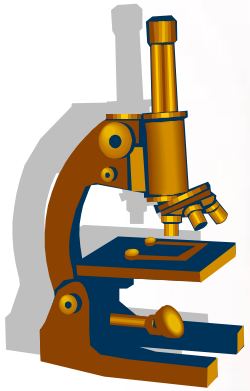
- **quality assurance and quality control**
- **repeatability (precision under repeatability conditions.)**
- **reproducibility (precision under reproducibility conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in different laboratories by different operators using different equipment)**
- **limit of detection (degraded by sample colour/turb)**
- **control charts**
- **target value chart (with fixed (pre-set) rather than statistically derived limits)**



MCERTS for test kits

- **The Environment Agency is in the process of considering the development of a separate MCERTS standard specifically for water test kits.**
- **It could be along the lines of the existing "Performance Standards and Test Procedures for Portable Water Monitoring Equipment" MCERTS standard**
- **Test kit manufacturers are being consulted on this issue**

2) Sampling issues



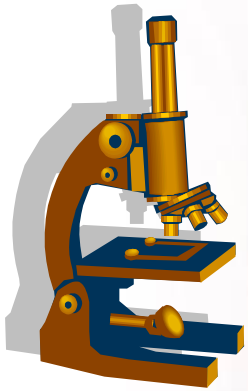
Key Criterion for Sampling & Analysis

All samples and results should be fit for the intended purpose

General Sampling Issues

- Appropriate training and documentation
- Appropriate sample containers
- Correctly taken fully representative samples
- Spot samples; time or flow weighted composite samples.
- Appropriate preservatives and storage if relevant
- Avoidance of contamination whilst taking the sample
- Need for appropriate trip blank samples

3) Analysis issues



Colorimetric methods

Visual comparison systems

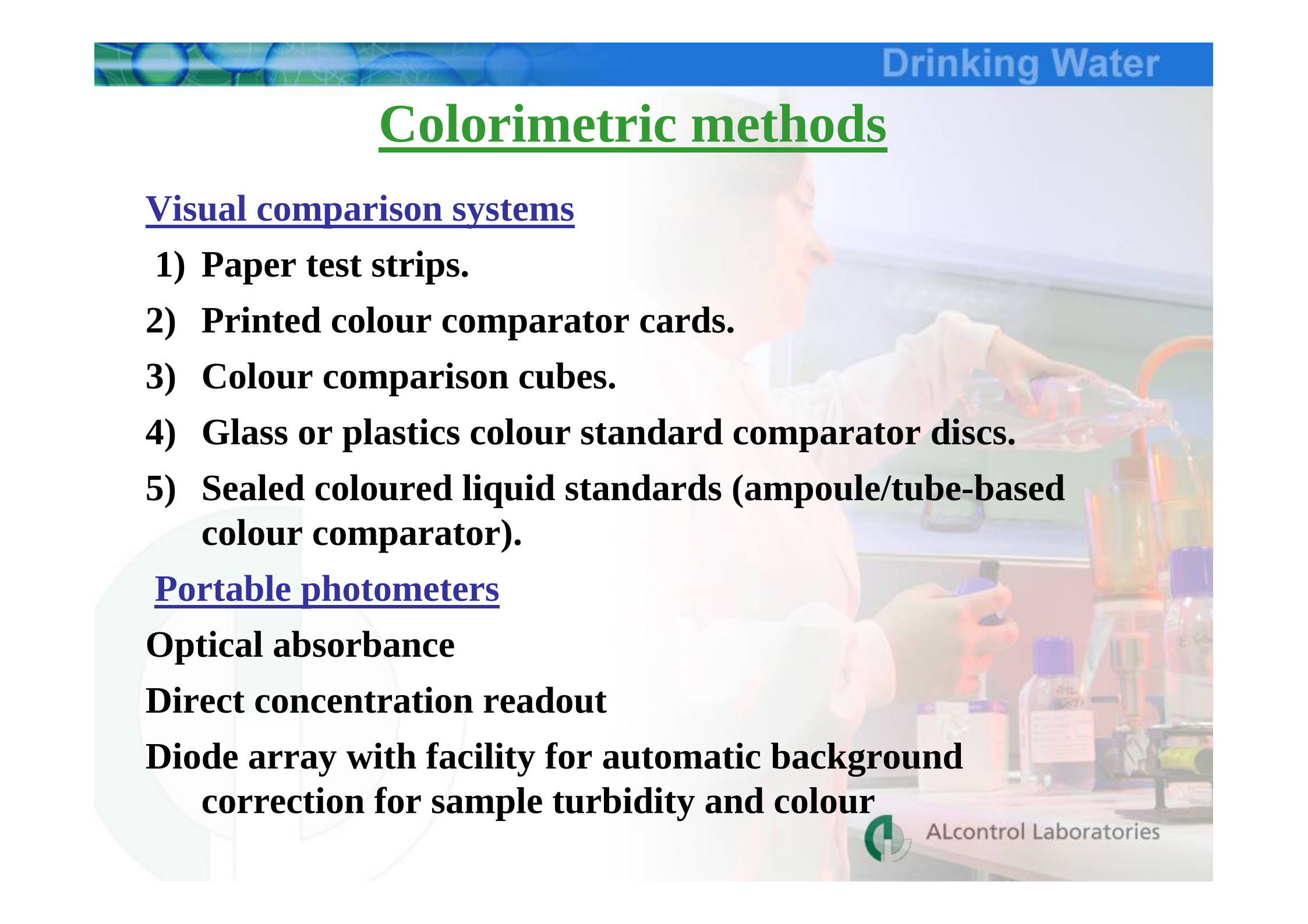
1) Paper test strips.
2) Printed colour comparator cards.
3) Colour comparison cubes.
4) Glass or plastics colour standard comparator discs.
5) Sealed coloured liquid standards (ampoule/tube-based colour comparator).

Portable photometers

Optical absorbance

Direct concentration readout

Diode array with facility for automatic background correction for sample turbidity and colour

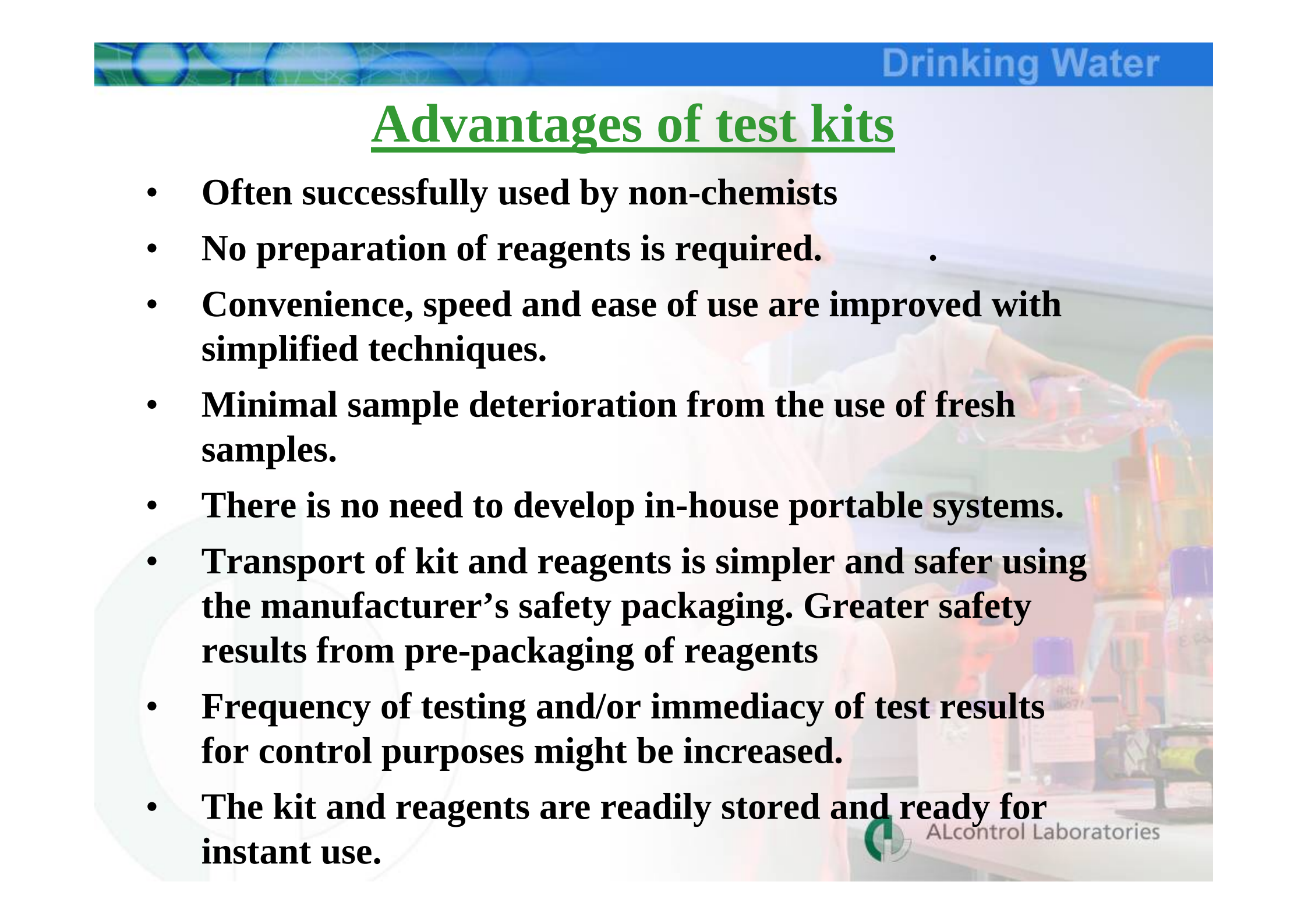


Titrimetric methods

- **Tablet count procedure**
- **Drop count procedure**
- **Digital titrators, with the titrant supplied in disposable plastics containers to fit the titrators**
- **Reverse Titration**
  The indicator solution and reagent is contained inside a vacuum-sealed, self-filling ampoule. A flexible valve assembly is attached to the tip of the ampoule. The tip of the ampoule is snapped with the valve assembly in place The tip of the valve assembly is then immersed in the sample (using an a simple manual suction valve), and small amounts of sample are drawn into the ampoule

Advantages of test kits

- **Often successfully used by non-chemists**
- **No preparation of reagents is required. .**
- **Convenience, speed and ease of use are improved with simplified techniques.**
- **Minimal sample deterioration from the use of fresh samples.**
- **There is no need to develop in-house portable systems.**
- **Transport of kit and reagents is simpler and safer using the manufacturer's safety packaging. Greater safety results from pre-packaging of reagents**
- **Frequency of testing and/or immediacy of test results for control purposes might be increased.**
- **The kit and reagents are readily stored and ready for instant use.**



Disadvantages of test kits

- **Cost per test might be higher especially when using the more advanced commercial test systems.**
- **The within batch and between batch reliability of test-kits for relevant matrices not always available from manufacturers.**
- **Accuracy and reliability of the test-kits are probably inferior to reference test methods undertaken within a laboratory. However, they should be able to provide results of adequate accuracy and meet the principle of "fit for the intended purpose required". It is the responsibility of the user to ensure that this is the case. (e.g. COD with test kits has an ISO standard BS ISO 15705:2002 is now the most commonly employed COD method in the UK)**
- **Interferences might be incompletely documented and biased results might then be observed for some sample matrices. Some test kits do, however, document the most common interferences.**

Main causes of 'unfit for purpose' results

- ***Incompetence of the operator (need for competence training).***
- Matrix interferences (although the initial method validation should indicate if this is a potential problem, it is not always possible to cover all potential extreme sample matrices that might be encountered for individual users).
- Inappropriate method/test-kit employed (need a validated test-kit method that meets the client performance targets).
- Contamination (need for principles of good laboratory practice to be understood and employed).
- Inappropriate sampling protocol and sample pre-treatment (this needs to be agreed with the client).

Demonstration of fitness for purpose

- Calibration
- Qualification (collection of all documented evidence)
- Validation
- QC checks
- System suitability checks (SSCs) which includes analytical instrument qualification

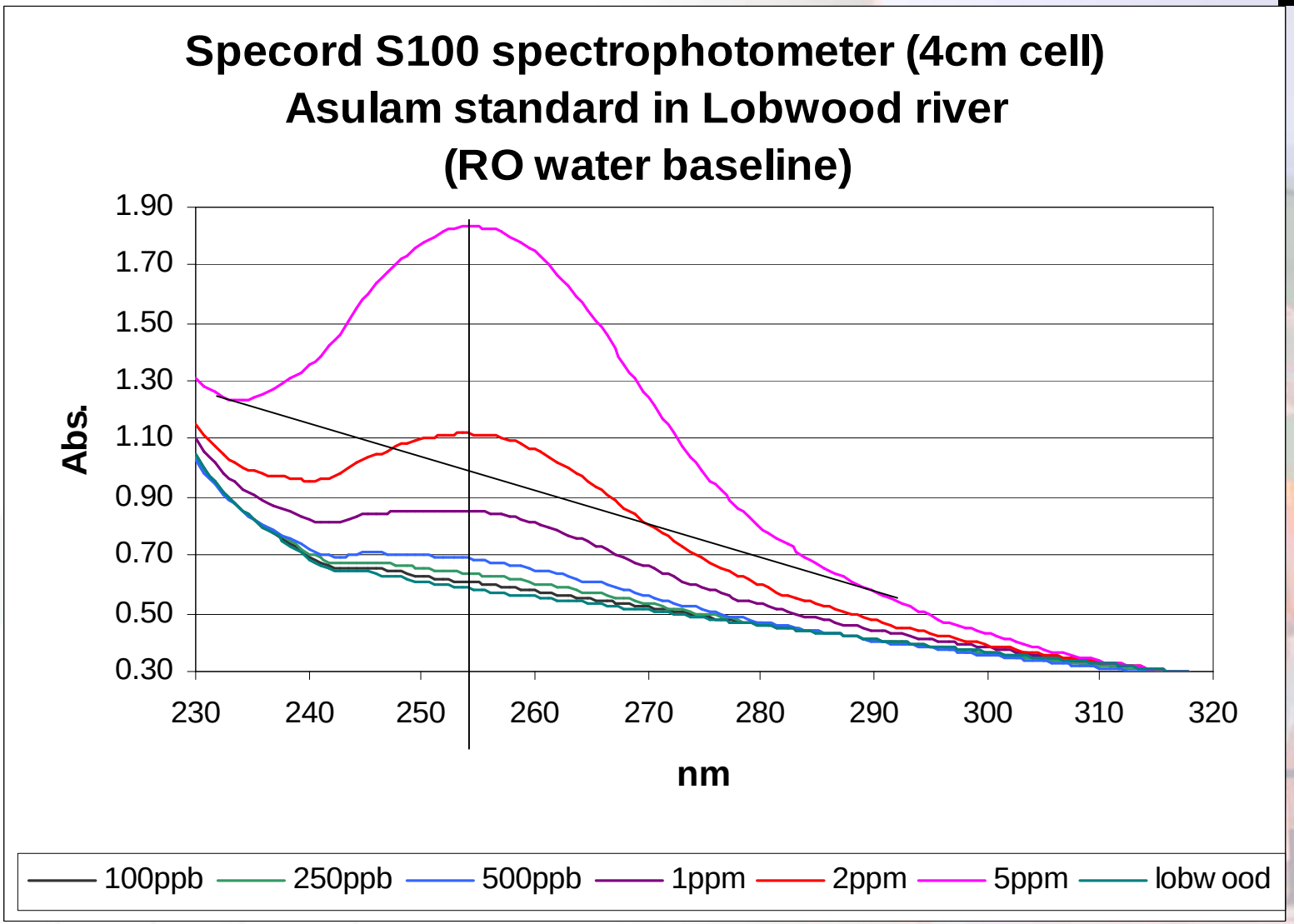
Interference considerations (1)

- Because of the wide range of water types covered in this British Standard the information given on interferences is not comprehensive. There is ***always*** the possibility that the water under test might contain substances which will interfere with the test procedure.
- One of most common form of interference, particularly for colorimetric test methods, is turbidity, which can easily be identified. The removal of turbidity and the manner of its removal is dependent upon local conditions
- Another is sample colour (e.g. presence of humic/fulvic acids)
- At low ambient temperatures some colorimetric methods have a greatly reduced rate of reaction.

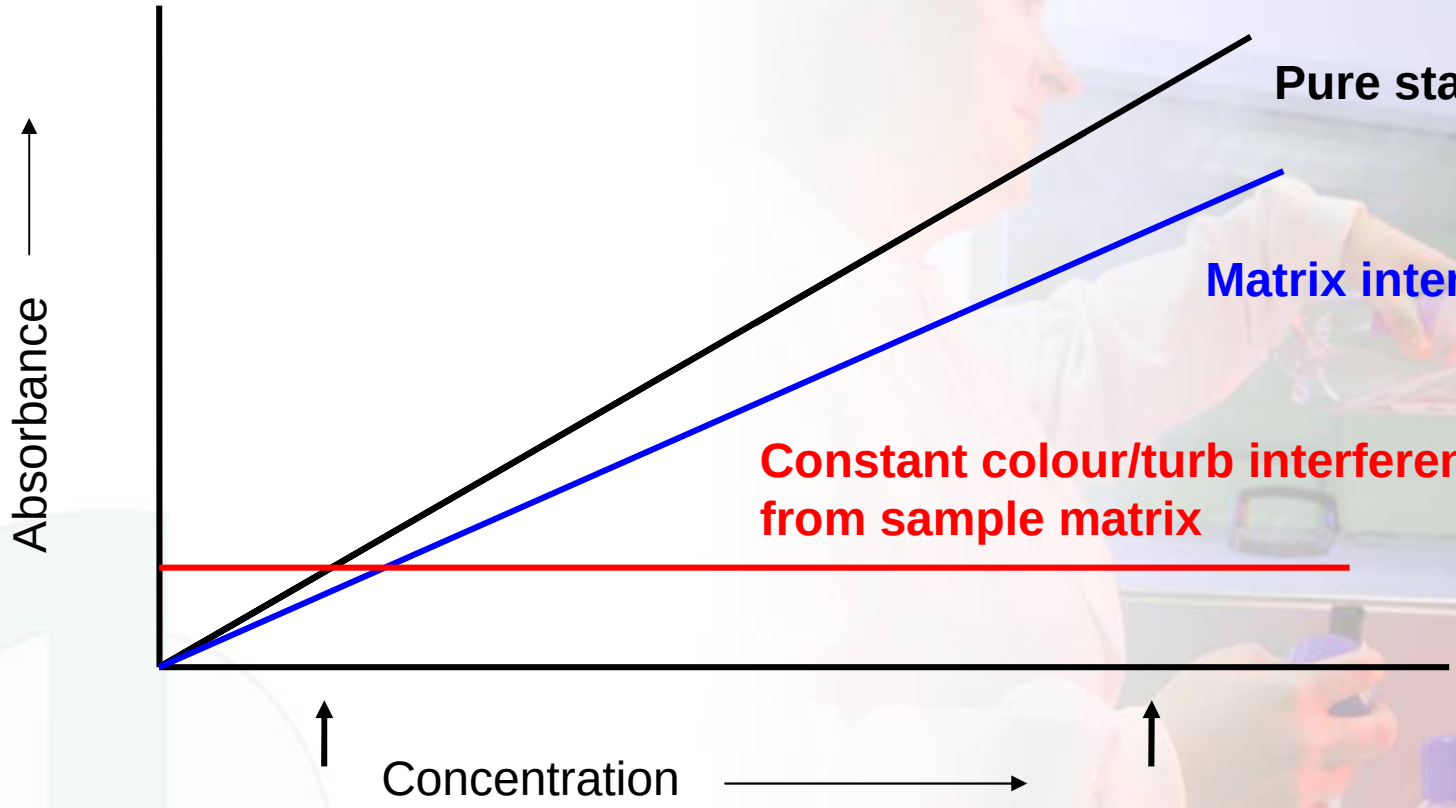
Interference considerations (2)

- Where the test method is similar or traceable to an existing ISO/CEN/British Standard, reference might be made to the standards for information on overcoming interferences.
- Pre-packaged reagents might include reagents designed to minimize or eliminate known interferences.
- Commercial test-kit systems might also indicate sample pre-treatment requirements designed to overcome interferences. Realistically, most of these need to carried out in a designated room/area testing facility

Effect of colour and turbidity



Effect of Matrix and Colour/Turbidity Interference



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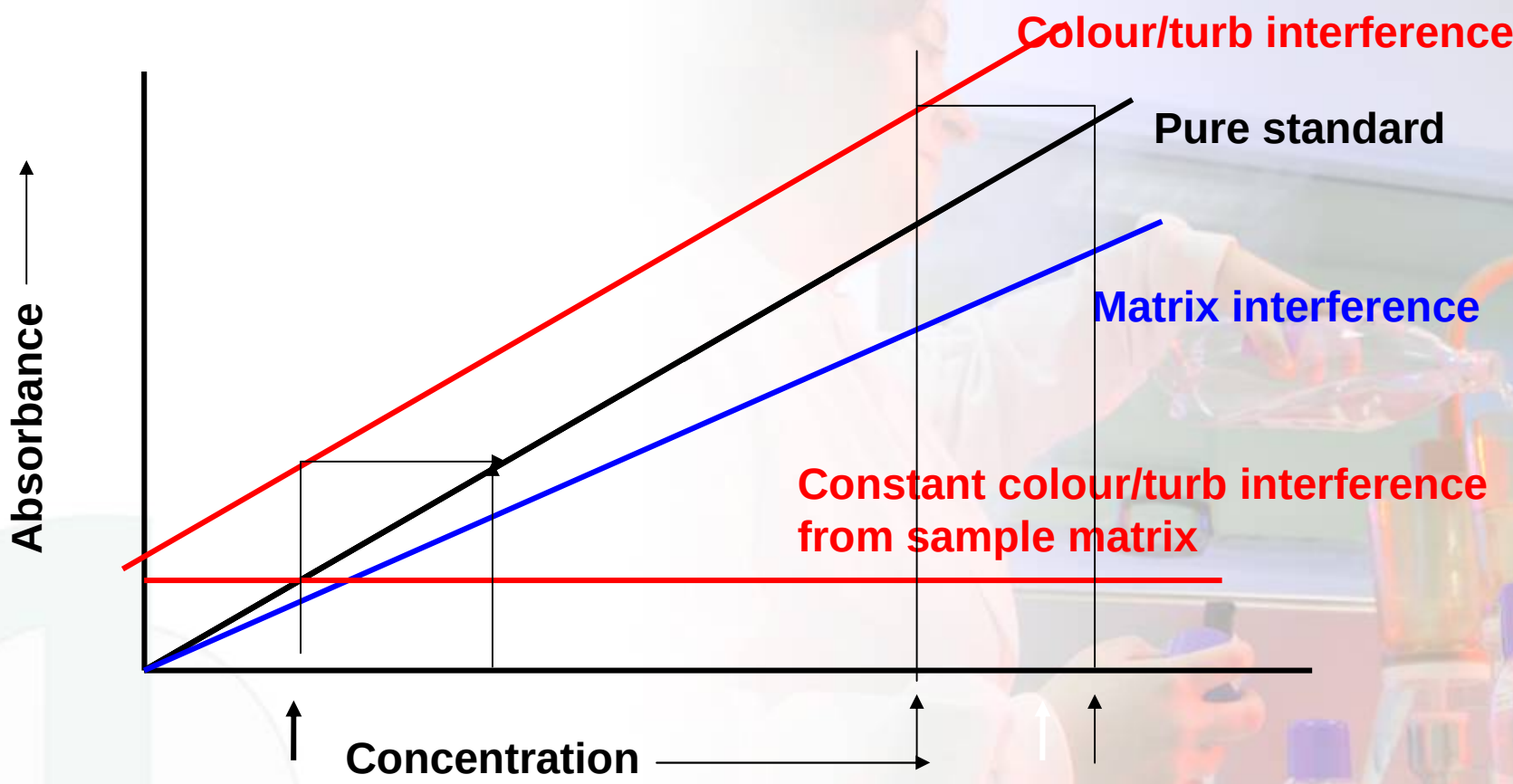
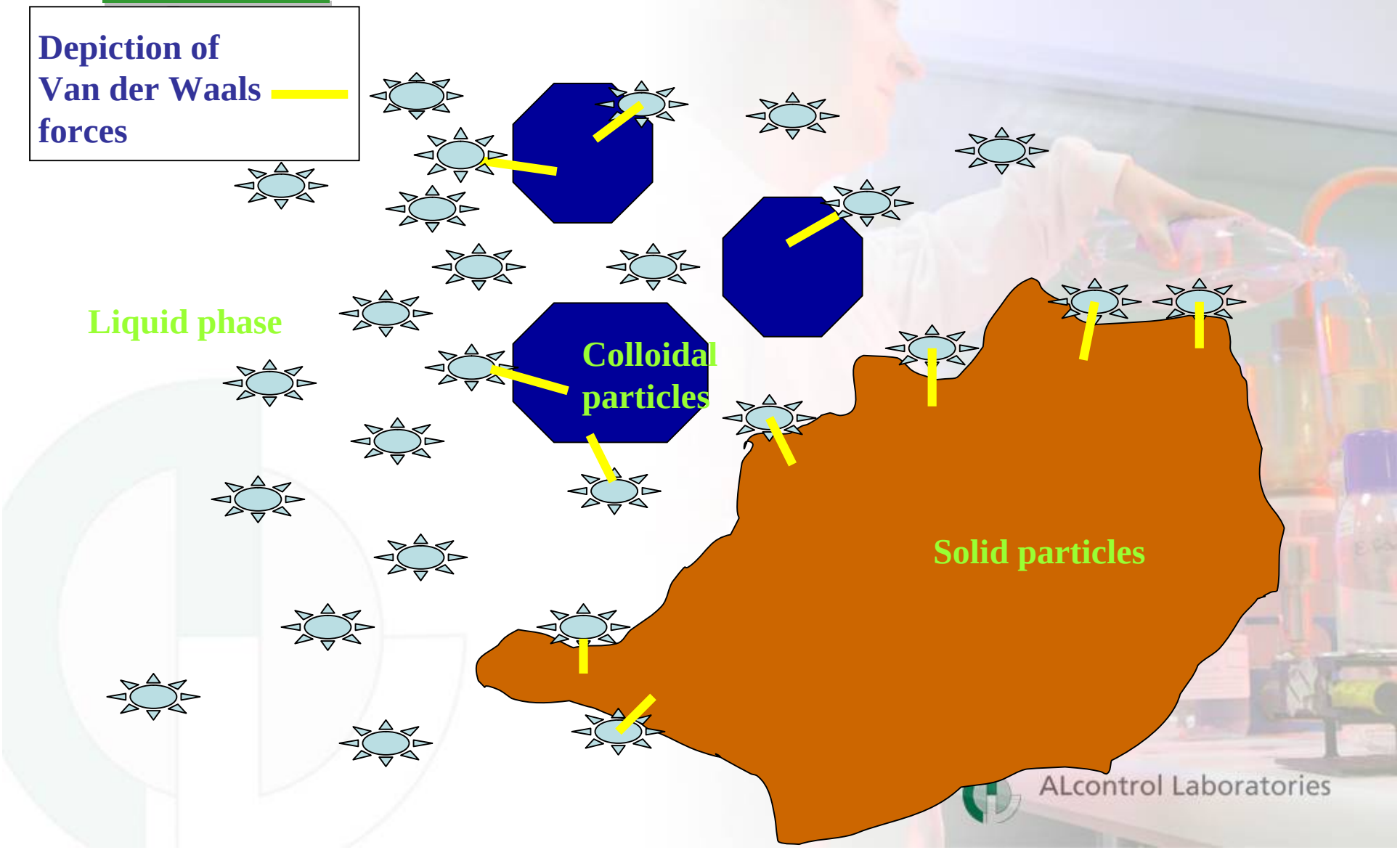


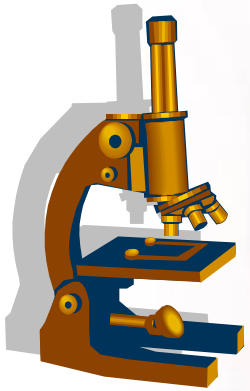
Distribution of Pollutants a in Water Sample e.g. Iron



Exotic Tests for Dedicated Test Room

- Adsorbable organohalogens (AOX)
- Total organic carbon (TOC)
- Total nitrogen
- Detergents (anionic; cationic and non-ionic)
- Phenol (extraction method)
- UV diode array

4) QA/QC issues



QA for test kit methods

- multiple testing;
- measurements of standards and possible reference materials;
- internal AQC, analysis of known samples or standards carried out with each batch of analysis and all the results are used to statistically control the procedure using Shewhart or equivalent charts;
- plausibility tests by means of dilution and standard addition;
- comparative tests with reference methods;
- interlaboratory tests; (proficiency testing);
- Documenting and regularly examining a control chart. Statistically derived or fixed (pre-set) limits

Documentation of test kit methods

- All test-kit methods should be fully documented by the test-kit users and include how to take a representative and relevant sample, QA/QC procedures, relevant simple system suitability checks (SSCs) and should also include the author, version number of the documentation and the method approval date.
- SSCs are simple tests to ensure that the associated test-kit instrumentation is functioning within specified limits **before** commencing analysis
- Each step in the method should be described sequentially and in full, should be unambiguous and written as simply as possible.

Documentation of test kit methods (1)

- Relevant QA/QC protocols need to be drawn up by the test-kit user for their particular application.
- Users should not rely on basic test-kit instructions alone, they might need to be rewritten to cover the context of the particular application and need to include sampling, sample preservation if required and sub-sampling and sample pre-treatment; all QA/QC aspects; as well as health and safety considerations with respect to the test-kit, and disposing of any waste after carrying out the test.
- The test method supplied with the kit should form the basis of the method. All method documentation should be fully traceable and signed off by a responsible experienced person.

Documentation of test kit methods (2)

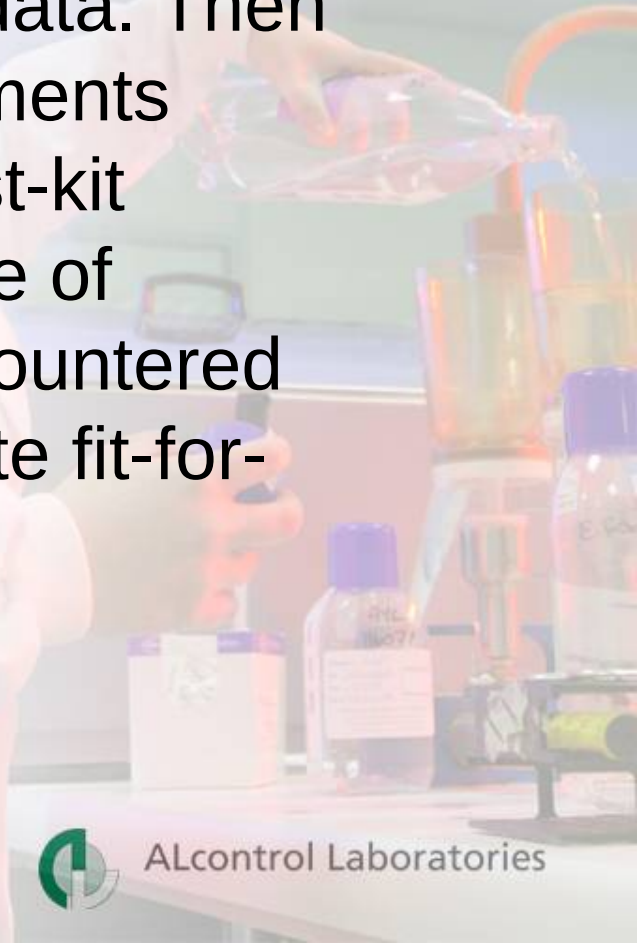
- Consideration should be given to laminating documented methods used in the “outside environment,” so they can more readily withstand adverse environmental conditions. Also this will assist in preventing unapproved amendments being subsequently added.
- It is the responsibility of the organisation/person carrying out the test method to ensure that it is capable of producing results meeting the performance requirements of the client

Target test-kit requirements (1)

- Before selecting a test-kit for a given parameter, users should carefully consider with the users of the data, the target requirements (including sampling considerations and performance characteristics) that are needed to obtain fit-for-purpose results in all sample matrices likely to be encountered.

Target test-kit requirements (2)

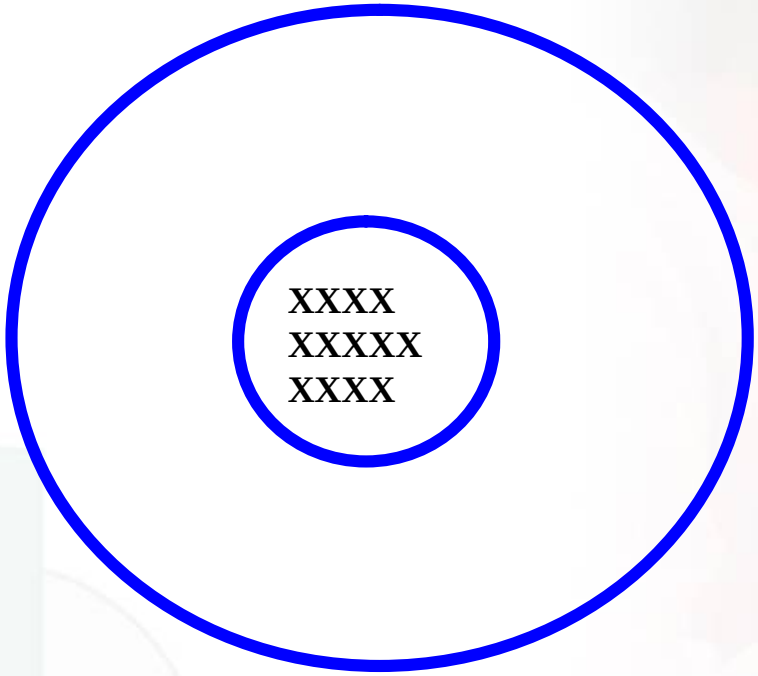
- These requirements should then be carefully documented and formally agreed with the final end user(s) of the data. Then the test-kit performance requirements should be discussed with the test-kit supplier with respect to the range of sample matrices likely to be encountered to help ensure that an appropriate fit-for-purpose test-kit is employed.



Manufacturer cited 95% confidence limits

Parameter	Concn	Confidential interval
	mg/litre	± mg/litre
Ammonium (as N)	4.00	0.25
Chloride	25	6
COD	80	12
COD	750	75
Iron	1.00	0.15
Nitrate (as N)	9.00	0.9
Orthophosphate (as P)	0.80	0.08
Orthophosphate (as P)	8.00	0.7
Sulfate (as SO_4)	100	15
Sulfate (as SO_4)	500	75

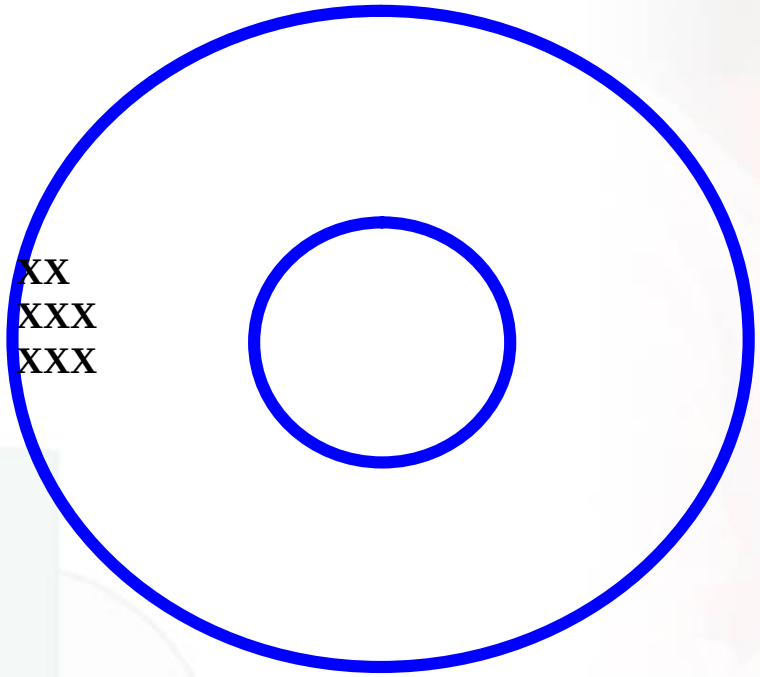
GOOD PRECISION, NEGLIGIBLE BIAS



True result	Actual results
10	9.8
	10.2
	9.9
	10.1
	10.0

Desired Analysis Results

GOOD PRECISION, SIGNIFICANT BIAS

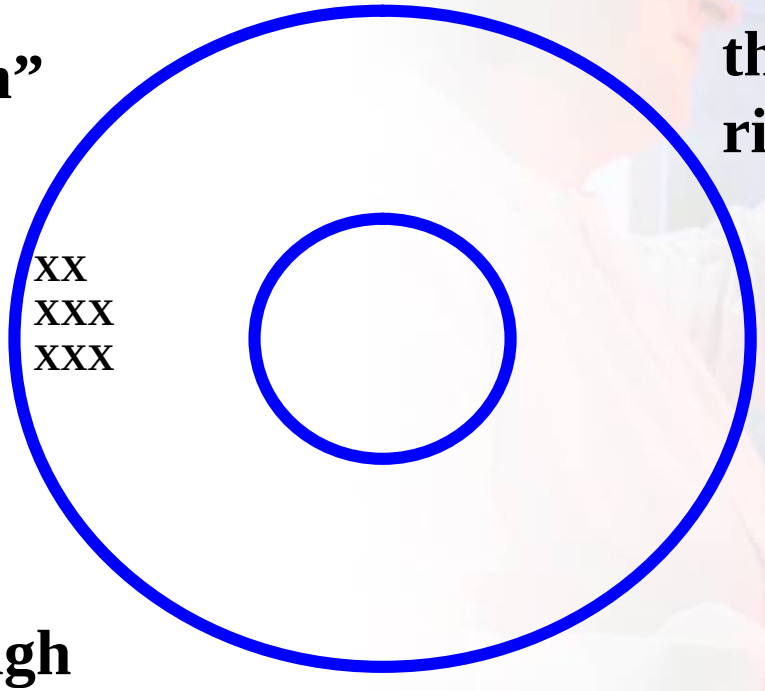


True result	Actual results		
10	3.8		
	4.2		
	3.9		
	4.1		
	4.0		

Effect of Poor Method Bias

GOOD PRECISION, SIGNIFICANT BIAS

"Precise Rubbish"



"The repeat analysis result is the same therefore it must be right"

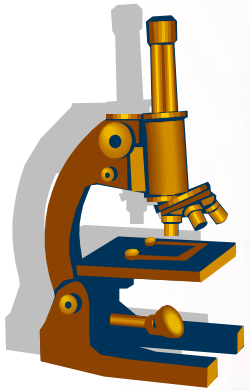
WRONG!!!

Do not equate high precision with accuracy

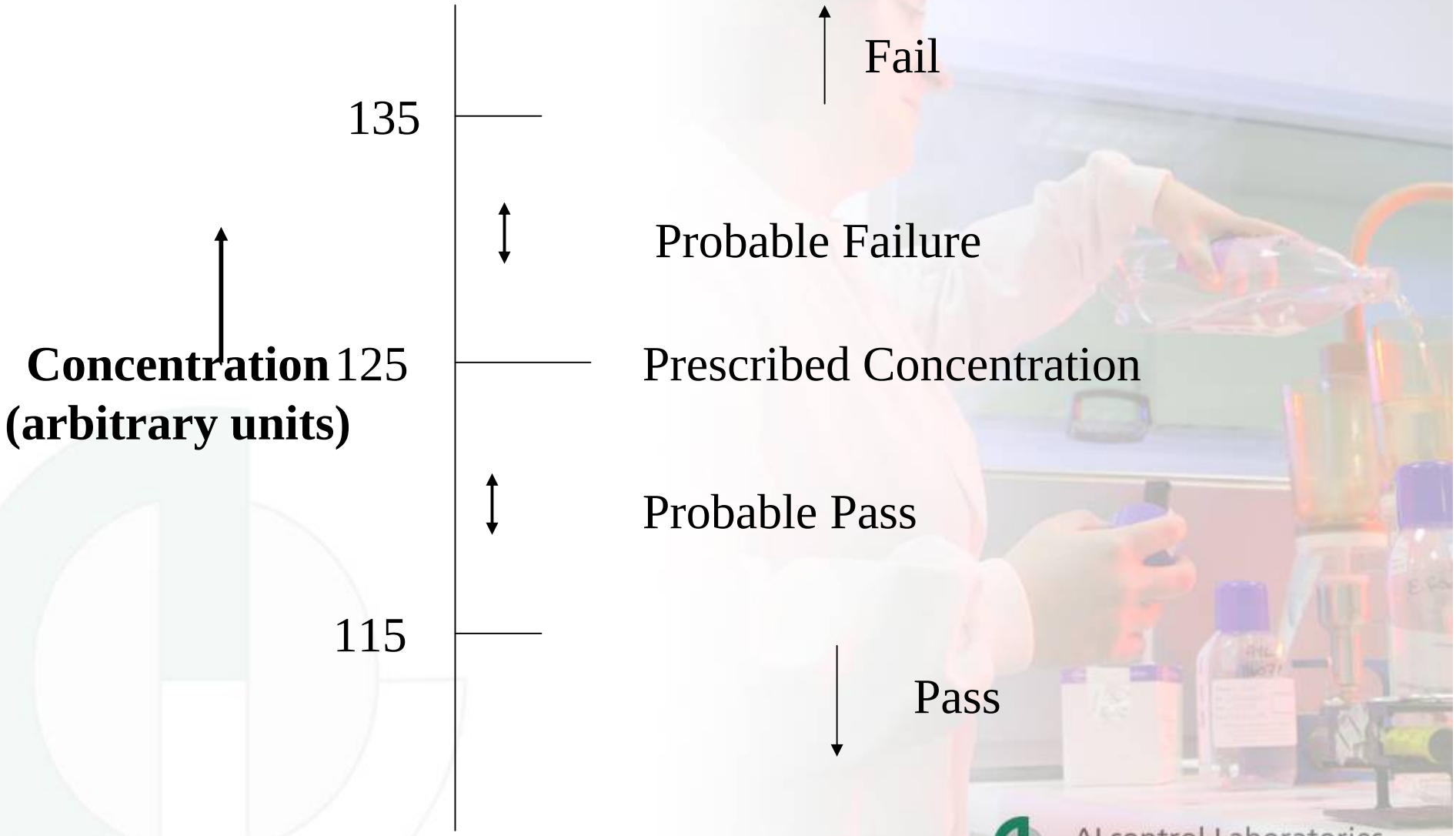
The more complex the sample matrix, the larger the likely bias

Effect of Method Bias

5) Regulatory issues



Result Confidence Limits COD UWWTD



Using the correct range test kit for COD

- The UWWTD final effluent COD limit is 125 mg/litre
- Most test kit manufacturers supply 0 -150 and 0 – 1500 mg/litre range COD test kits
- Some labs to save time and money just use the 0 - 1500 mg/litre range for both crude sewage and final effluents
- **Using a 0 – 1500 mg/litre range test kit to monitor a 125 mg/litre critical COD consent limit is bad practice!!!**
- 125 mg/litre is 8.3% of the analytical range

Using the correct range test kit for COD

VWR International Ltd, 05 February 2002

•Please see attached documents referring to the Merck manufactured COD cell test range **10-150 mg/l**. VWR International Ltd on behalf of Merck KgaA would always recommend the use of the aforementioned range when carrying out compliance testing according the most recent Urban Waste Water Directives. **The attached data clearly shows that the narrower the COD ranges the more accurate and reliable the results will be and that working around the 125 mg/l level the 10-150 range is the most suitable.**

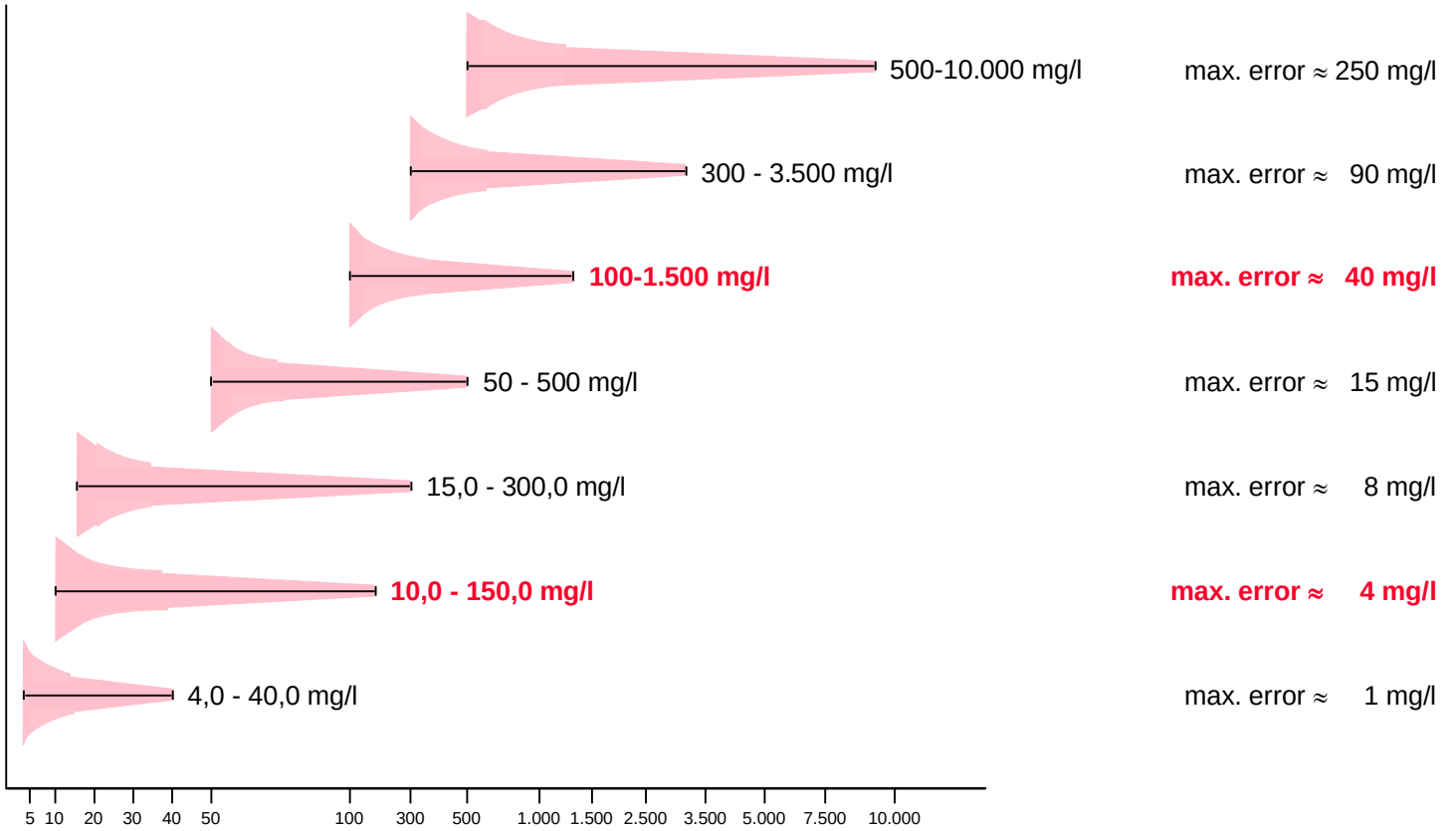
Extensive testing was done in Germany to generate this data using many samples and replicates. **Merck KgaA would strongly suggest any potential user of COD tubes to try and choose a range that would result in the sample appearing mid to upper range thus giving a "truer" result than may be obtained from manufacturers who do not provide seven ranges of COD cell test.**

Optimum test kit concentration range issue

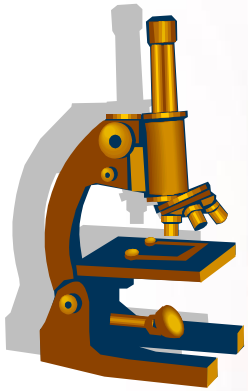
Quality of the COD determination

the maximum error is 5 % in the mid range of each test

M
MERCK

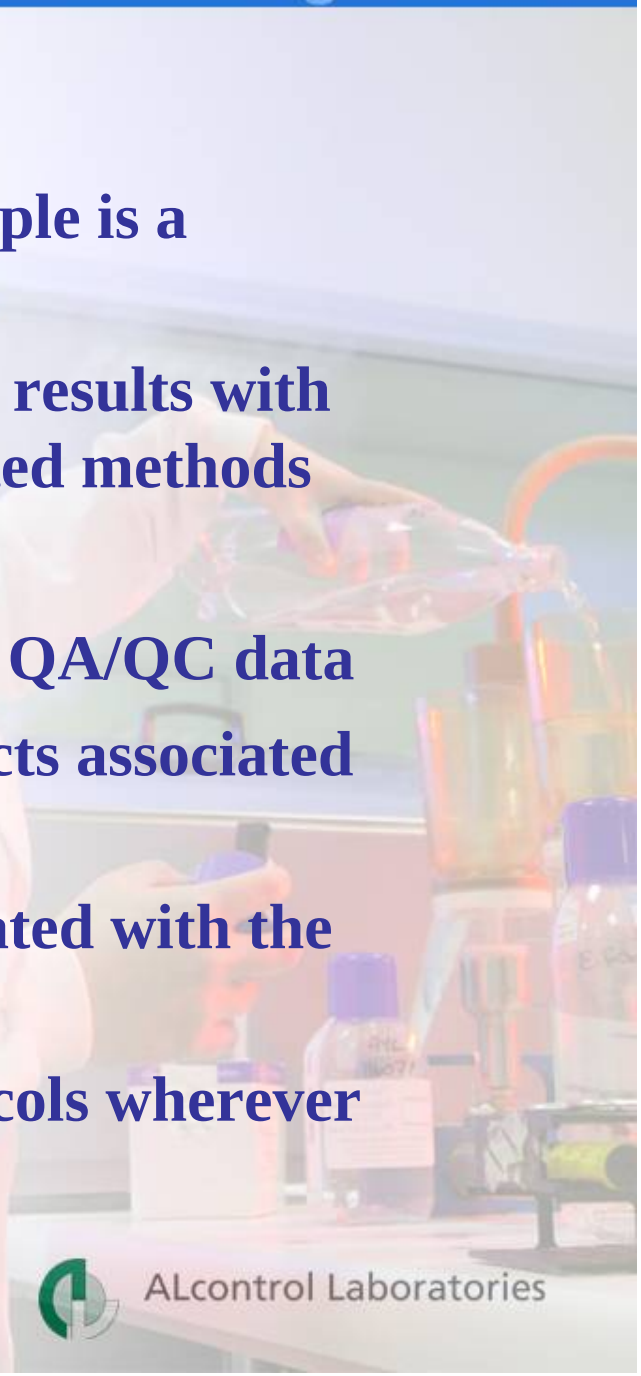


6) Conclusions



Conclusions

- Analysing an inappropriately taken sample is a complete waste of time
- Modern test kits can give fit for purpose results with suitably trained staff and well documented methods
- Appropriate QA/QC is key to this
- Fully document all methods, results and QA/QC data
- Be aware of significant interference effects associated with the analysis of all relevant matrices
- Be aware of the confidence limits associated with the analysis
- Validate all methods as per NS 30 protocols wherever possible



The End!!!