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DRINKING WATER INSPECTORATE

WATER SUPPLY (WATER QUALITY) REGULATIONS 2000 / 2001

REPORT ON THE RESULTS OF THE SURVEY OF ANALYTICAL PERFORMANCE FOR THE MEASUREMENT OF LEAD

Home Page: www.dwi.gov.uk
E mail: dwi.enquiries@defra.gsi.gov.uk

Department for Environment,
Food and Rural Affairs

Cynulliad Cenedlaethol Cymru
The National Assembly for Wales

A report on the results of the survey of analytical performance for the measurement of lead within the laboratories of English and Welsh Water Companies.

By Peter Walker – Technical Consultant

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1.0 Executive Summary

1.1 The survey had good response from the majority of the water companies, with only a few examples where incomplete data was supplied against the specification. The quality of the supplied data was again generally good, with very few examples of ambiguously written procedures, but with more documents that had been photocopied to produce poor copies, difficult to read and interpret.

1.2 The survey covered all commonly used analytical methods involving spectrometry i.e. Atomic Absorption, Inductively Coupled Plasma – both OES and MS, but none involving electrochemical methods. It indicated that all instrument/method combinations would meet the required specifications for a 25ug Pb/l PCV, and that most would meet the lower 10ug/l plumbosolvency monitoring regulations.
At the low concentrations being measured, small differences in trueness or precision can show up as significant changes in plumbosolvency optimisation data, which could lead to an erroneous conclusion that a real change has occurred. Site-specific samples should always be analysed using the same instrument or technique to minimise errors. This is critical where instruments utilising different techniques are used in the analysing laboratory, or when similar instruments show significant analytical performance differences. Changes to instruments or methodology should only be made for good reason and the timing of the change clearly recorded. Ideally a period of overlap when all samples are analysed using both systems should be employed. This is particularly important for AAS-ETA methods where there can be a marked difference in the errors induced by matrix effects for different instruments and methods.

1.3 The variation of analytical ranges used was surprisingly large for a parameter whose control limit is effectively 10 ug/l. This variation was also seen in the concentrations of the external calibration solutions used to calibrate the method. The increased use of single stage large dilutions involving small initial aliquots was also noted. The use of initial daily performance checks against formal documented criteria was widespread, although variation in specific actions was noted.

1.4 A small number of peculiarities were detected in validation protocol and in the operation of the Analytical Quality Control procedures. From the data supplied there is evidence that many validations are close to or beyond the recommended time limit for re-validation. This may be due to the recognition that the regulatory standards would change. However, when this happens there are opportunities for improvements to be made in the number and concentration of the standards and sample/spiked samples used. Improved long term monitoring of method performance at the control limit requires more realistic target AQC values than indicated in this data. External AQC data was

generally good, but there were some anomalous results that defy explanation.

1.5 The instruments were maintained in good condition, all having at least one Preventative Maintenance visit per year. Some initial problems with peripheral equipment for ICP-MS instruments, mostly water chillers for temperature control, were noted – but no other common recurring problem could be detected from the supplied data.

Conclusions

From the survey information provided the following information can be deduced;

- Most users of ICP-MS and AAS-ETA techniques have the capability to meet all the requirements of the Regulations reducing the PCV to 25ugPb/l, and to satisfy the needs of plumbosolvency monitoring.

- Some ICP-OES users will meet the new PCV limit, but are unlikely to comply with the plumbosolvency monitoring requirements.

- Re-validation will be needed for most users. Opportunity should be taken to review analytical range and allocation of calibration standards within the chosen range, using the NS30 protocol fully.

- The target concentration for AQC standards should be aligned to the new 25ug Pb/l PCV, or to the 10ug Pb/l plumbosolvency limit, as appropriate.

- The use of system suitability checks and regular routine/PM maintenance are essential to ensure instruments are “fit for purpose”, prior to analysis.

2.0 Introduction.

2.1 Lead is a persistent and accumulative toxic metal that is being reduced in the environment by action on many previously common uses. The detrimental effect to the intelligence of growing children by persistent low-level exposure has been proven by many studies, and many national and international policies are directed to reducing or removing exposure to this poison.

2.2 The reduction in the Prescribed Concentration or Value (PCV) for lead from 50ug/l to 25ug/l, is part of this strategy, as is the use of plumbosolvency control measures to reduce the dissolution of lead from existing lead supply pipes. These new regulations impose on the

analytical laboratories of water companies a new requirement for increased precision and trueness in the data produced for lead. It is the plumbosolvency regulations that set the standard for compliance – effectively reducing the PCV to 10ug/l now rather than in 2013, for analytical laboratories.

2.3 The results of this survey are based on the requirements for analytical testing specified in information published by DWI. Precision is defined as twice the Total Standard Deviation from Validation performance testing to NS30 protocol. Trueness is the difference between the true concentration and the actual value obtained. Recovery in this report is quoted as % Trueness, wherever the values are available for calculation.

2.4 Analysis of water samples for lead at, or below the 10ug/l concentration involves limited choice of technique. Voltametry or spectrometry are realistically the only options available to water company laboratories. No laboratory uses voltametry – presumably due to its slow throughput. The majority of laboratories favour the use of ICP-Mass Spectrometry, while some use “Atomic Absorption Spectrometry – Electro-Thermal Atomisation” (AAS-ETA or AAS-furnace). There are few users of ICP – OES, but none in combination with Ultrasonic Nebulisation (USN) to enhance the technique.

3.0 Practical considerations

3.1 Sampling and pre-treatment

3.1.1 Correct sampling is a necessary part of the analytical procedure. The survey showed that samples are being taken into plastic containers. Some of these are pre-acidified, while most are acidified on receipt in the laboratory. Final acid concentration varies slightly, but all will be sufficient to retain the lead in solution.

3.1.2 Sample pre-treatment varies between laboratories. For some, the clear, bright samples are left acidified for a specified time at ambient temperature to complete dissolution, utilising digestion only with turbid/coloured samples. Other laboratories digest all samples routinely.

BS EN ISO 5667-3:2003 advises that if samples are not preserved at the time of sampling, metals and metallic compounds can precipitate out of solution and dissolved metals or metals in a colloidal state can be irreversibly adsorbed onto the surface of the container or solid materials in the samples. To prevent these effects it is recommended that samples are acidified to between pH 1 and pH 2 with nitric acid at the time of sampling. Companies are expected to follow this advice.

Insoluble lead salts, possibly with elemental lead attached, may be present in samples, especially where plumbosolvency control is practised and the system is either not optimised or there are problems with either pH control or orthophosphate dosing. Such particles may not be visible to the naked eye even in transparent sample containers. Companies are therefore expected to pre-treat all samples for lead analysis to ensure that all lead in the sample is taken into solution. Appropriate pre-treatment procedures are given ISO 15587-1:2002 and ISO 15587-2:2002. Companies will be expected to demonstrate that any alternative used will dissolve all the lead present in any particulate material which may be present in samples.

3.1.3 Some laboratories add extra calcium and magnesium ions to match the matrix of standards to samples, while some ICP-MS users spike with Internal Standard solution at this stage. Some AAS-ETA users also add matrix modifiers.

3.2 **Analytical range**

3.2.1 The current users of AAS-ETA recognise the limitations of the technique and have restricted the analytical range used to 30ug/l maximum.

3.2.2 Those laboratories using ICP-OES have opted for larger ranges, up to 1000ug/l. The need for this is presumably due to the low emissions from lead in the plasma, although for plumbosolvency work the working range is within the first 1% of the analytical range.

3.2.3 The largest variation in analytical range is to found within the users of ICP-MS instruments. The smallest range is 0 – 12 ug/l, whilst the largest is 0 – 400 ug/l. Most users opt for either 0 –100 ug/l or 0 – 200 ug/l.

3.2.4 It is not expected that the raw or supplied water would ever have these concentrations of lead within them, therefore it is concluded that these ranges have been chosen to allow one instrument to analyse a variety of sample types that can be found in multi-functional water company laboratories. It is recognised that the ICP-MS technique is linear over several orders of concentration, however this advantage can only be fully appreciated if suitable calibration standards are employed. Good laboratory practice should be to use enough calibration standards to adequately cover the analytical range – ensuring that at least one standard falls within the area of the analytical range where either most results occur or that a regulatory compliance limit exists. It is recommended that this practice is used when analysing samples for lead under the new requirements.

3.2.5 It is noted that a significant number of laboratories fail to use a calibration standard of 10ug/l or below.

3.3 **Preparation of calibration and AQC standards**.

3.3.1 To fully utilise the linearity, or otherwise, of a technique it must be calibrated over a suitable range for its use. The preparation of standards to fulfil this calibration must therefore be of the highest accuracy to enable accurate and consistent setting of the analytical instrument over time. The use of “A” grade glassware was promoted for this purpose, as its tolerances were known. To minimise errors, many-stage serial dilutions were carried out to obtain accurately known final concentrations of the standards.

3.3.2 It is noted from the survey responses that some laboratories use glass or plastic volumetric equipment that does not comply with Grade “A” specification for standards preparation. It is also noted that many laboratories use a single wide-range dilution involving the dilution of a small initial aliquot to a large final volume as a substitute for serial dilution. In most instances this occurs in the first step of dilution from the 1000mg/l commercially available standard to an intermediate stage standard.

3.3.3 These practises are not recommended as they can lead to systematic errors being introduced into the standards. Due to the greater tolerances involved with non-Grade A volumetric glassware, the dilution will not be as precise and greater variation will occur between batches. Wide-range dilution will also introduce systematic error into calibration, as there exists greater possibility for volume derived, and incomplete mixing errors to occur.

3.3.4 These systematic errors will be maintained for extended periods, as the stated shelf life for some of these standard solutions is quite long.

3.3.4 The effect of these practices can be seen in the extended occurrence of low-level bias that exists in the Shewhart charts provided.

3.3.5 It is imperative that these errors are minimised when working with the very low concentrations of lead found in raw and treated waters. It is recommended that Water Company laboratories review the practices they use and adopt the use of Grade A glassware and serial dilution to prepare calibration and AQC standards.

3.4 Variability control strategies.

3.4.1 All analytical methods have inherent variation, due to the combination of systematic and random errors that occur during the measurement. Validation to NS30 protocol tests the analytical procedure and estimates these errors.

3.4.2 The users of AAS-ETA for lead analysis all use a matrix modifier to overcome systematic error. Different compounds at different concentrations are used between laboratories. Additionally, multiple replicate analysis is carried out by all users to minimise random error.

3.4.3 Modern ICP-MS instruments have software-controlled facility to take multiple readings from the plasma during the nebulisation period of a sample. These individual readings are averaged and the standard deviation calculated. In most instances the information on instrument set-up was not provided in the responses. It is recommended that a minimum of three, and preferably, five replicate samplings from the plasma per solution under test are made to produce the result reported.

3.4.4 All ICP-MS users use internal standards to compensate for temperature and matrix effects during analysis. Three main elements are used for internal standards – ^{209}Bismuth, ^{205}Tellurium and ^{103}Rhodium, with ^{115}Indium used by two laboratories. All are stable isotopes. Theoretically, the closer the mass of the internal standard is to that of the parameter being determined, then the better effect would be expected. However, despite the mass difference between rhodium/indium and lead, all appear to function well.

3.4.5 At the low concentrations being measured, small differences in trueness or precision can show up as significant changes in plumbosolvency optimisation data, which could lead to an erroneous conclusion that a real change has occurred. Site-specific samples should always be analysed using the same instrument or technique to minimise errors. This is critical where instruments utilising different techniques are used in the analysing laboratory, or when similar instruments show significant analytical performance differences. Changes to instruments or methodology should only be made for good reason and the timing of the change clearly recorded. Ideally a period of overlap when all samples are analysed using both systems should be employed. This is particularly important for AAS-ETA methods where there can be a marked difference in the errors induced by matrix effects for different instruments and methods.

3.5 Validation and Analytical Quality Control (AQC)

3.5.1 It was surprising to note that despite the quality of reference documentation existing on both subjects there were still poor scientific practices detected within the response documentation.

3.5.2 Validation should be organised such that sufficient standard solutions are used to cover the range of analysis. The samples and spiking of those samples should encompass the range of sample types processed by a laboratory and at concentrations appropriate to the limit values in force or anticipated. These samples would be replicated and

then the order of analysis randomised to present differing profiles of concentrations to the instrument, anticipating conditions normally found when analysing real samples. Statistical processing of the data from this exercise produces performance information on the analytical system. The information gained from this exercise is used to establish if the procedure is compliant with minimum regulatory performance standards and to establish the benchmark for ongoing AQC monitoring. Responses showed that several laboratories did not randomise the validation samples and thus compromised the performance data by analysing in sequence of progressive increasing concentration. Good practice indicates that validation is repeated approximately every three to five years – this was not always followed.

3.5.3 It is recommended that when re-validation occurs, that the opportunity is taken to also include a phosphate treated water for sample/spiking analysis. This sample should be representative of supplied waters that are subject to phosphate addition for plumbosolvency control.

3.5.4 AQC is the process of monitoring the ongoing performance of the analytical system following validation. The data produced from individual AQC standards indicates whether the associated sample results are valid or not, while statistical analysis of the data set shows variation in system performance over time. The interpretation of the rules for AQC varied between laboratories, some using multiple concentrations of AQC standards within a single batch, others using single standards but with differing concentrations, depending upon the laboratory. Some laboratories additionally operated Shewhart charts based on recovery or difference between duplicates. Most laboratories regularly reviewed and updated the limits to the Shewhart charts based on standard deviation from the preceding data set, but there were some who appeared to operate charts based on percentage values – this is inappropriate.

3.5.5 It was noted that most laboratories use an AQC standard concentration above 25 ug Pb/l. While this reflects the previously higher PCV value, it is not appropriate for the new PCV limit nor for the 10ug Pb/l plumbosolvency requirements. It is recommended that when re-validation exercises are completed, then the AQC target concentration be adjusted downward to reflect the new limits.

3.5.6 Participation in external AQC is essential to establish if the analytical system will perform satisfactorily when presented with an unknown sample. Two schemes were used by the responding laboratories – Aquacheck and LEAP. Some laboratories participated in both schemes, while most subscribed to only one. Both schemes have advantages and disadvantages, but they offer good opportunity for performance assessment across a variety of sample types and concentrations. In most cases the results provided showed that good agreement was reached, but occasionally odd results were produced.

Documentation provided showed that in accordance with good practice, the factors producing the peculiar results were investigated and recorded.

3.5.7 These test solutions also offer the opportunity to test the precision of any auto-dilution facilities provided to bring an over-range sample within the calibrated analytical range.

3.6 System suitability checks

3.6.1 Most responses provided information on system suitability checks in use, while for most others it could be inferred from documentation provided. The users of AAS-ETA and ICP-OES operated a system where minimum raw signal criteria for a lead standard of fixed concentration had to be exceeded, prior to routine use.

3.6.2 ICP-MS operators predominantly used the facilities available from the software to establish “fit for purpose” criteria before use. This should involve analysis of a standard/standards with suitable concentration, plus minimising oxide and multiple ion formation by controlling plasma conditions. It is recommended that background counts, and some method of monitoring the sensitivity of the detector used for lead determination be undertaken prior to routine daily use. The criteria for acceptable performance should be set to an appropriate value that triggers a full “tune” of the instrument using internal diagnostics. It is not considered appropriate to rely upon a full tune once every set time period, if full analytical performance is to be maintained at the low concentrations being analysed. Detector deterioration is use dependant and should be monitored carefully.

4.0 Documentation

4.1 The documentation provided was individually highly varied but suitable in all cases.

4.2 For ease of reference, the practice of incorporating the daily, weekly and monthly routine maintenance programme within the analytical procedure should be adopted.

5.0 Conclusions

From the survey information provided the following information can be deduced;

- Most users of ICP-MS and AAS-ETA techniques have the capability to meet all the requirements of the Regulations reducing the PCV to 25ugPb/l, and to satisfy the needs of plumbosolvency monitoring.

- Some ICP-OES users will meet the new PCV limit, but are unlikely to comply with the plumbosolvency monitoring requirements.

- Re-validation will be needed for most users. Opportunity should be taken to review analytical range and allocation of calibration standards within the chosen range, using the NS30 protocol fully.

- The target concentration for AQC standards should be aligned to the new 25ug Pb/l PCV, or to the 10ug Pb/l plumbosolvency limit, as appropriate.

- The use of system suitability checks and regular routine/PM maintenance are essential to ensure instruments are “fit for purpose”, prior to analysis.

6.0 Recommendations.

6.1 Good laboratory practice should be to use enough calibration standards to adequately cover the analytical range – ensuring that at least one standard falls within the area of the analytical range where either most results occur or that a regulatory compliance limit exists. It is recommended that this practice be used when analysing samples for lead under the new requirements. (3.2.4)

6.2 It is recommended that Water Company laboratories review the practices they use and adopt the use of Grade “A “ or equivalent glassware and serial dilution to prepare calibration and AQC standards. It is imperative that these errors are minimised when working with the very low concentrations of lead found in raw and treated waters. (3.3.5)

6.3 It is recommended that a minimum of three, and preferably, five replicate samplings from the plasma per solution under test are made to produce the result reported. (3.4.3)

6.4 It is recommended that when re-validation occurs, that the opportunity is taken to also include a phosphate treated water for sample/spiking analysis. This sample should be representative of supplied waters that are subject to phosphate addition for plumbosolvency control. (3.5.3)

6.5 It is recommended that when re-validation exercises are completed, then the AQC target concentration be adjusted downward to reflect the new limits. (3.5.5)

6.6 It is recommended that background counts, and some method of monitoring the sensitivity of the detector used for lead determination be undertaken prior to routine daily use of ICP-MS instruments. The criteria for acceptable performance should be set to an appropriate value that triggers a full “tune” of the instrument using internal diagnostics. (3.6.2)