THE DRINKING WATER INSPECTORATE

SUMMARY REPORT ON THE 2004 NON MICROBIOLOGICAL AUDIT TRAILS

THE DRINKING WATER INSPECTORATE - NON-MICROBIOLOGICAL AUDIT TRAILS FOR 2004 CARRIED OUT BY DR PETER WHITTLE

Overall Summary and Conclusions

1 Introduction

1.1 During 2004 Dr Whittle, Temporary Inspector, undertook the annual non-microbiological vertical audits of all 26 water companies in England and Wales. A risk based approach was taken on the number of samples to be audited, based on the relative size of the company in terms of population supplied and findings from the 2003 audits. For the smaller companies just two samples were selected for audit, increasing to a maximum of 16 samples for the larger companies. In addition to this, three companies had extra samples included in their audit programme to meet specific local situations (see below).

1.2 Following discussions with Dr Whittle, the Inspectorate selected five key parameters for audit. These were residual chlorine, isoproturon, lead, benzene, and hydrogen ion. Chlortoluron was substituted where isoproturon was not scheduled for the chosen sample point. Two companies were audited additionally for nitrite because they changed their contract laboratory part way through the year and one company was audited additionally for mercury following a reported compliance failure in 2003. Between one and four samples were audited for each parameter, depending on company size.

1.3 A total of 215 samples were audited, an increase of 32 compared to the number audited in 2003. In terms of samples per parameter per company, this amounted to:

residual chlorine	all companies; 26 samples
isoproturon	15 companies; 56 samples
chlortoluron	3 companies; 3 samples
lead	24 companies; 62 samples
benzene	24 companies; 34 samples
hydrogen ion	15 companies; 32 samples
nitrite	2 companies; 4 samples
mercury	1 company; 1 sample

Most of the samples selected for audit were taken during 2004, although a few were from 2003. In order to see how well companies were responding to recommendations arising from the 2003 audits, Inspectors endeavoured to select samples taken after the company was first made aware of the recommendation. Unfortunately, given the timing of the audit programme, this was not always possible.

1.4 Individual reports were produced for each company. Dr Whittle made a total of **88 recommendations** on matters, which in his opinion, could result in a foreseeable risk of breaching a regulatory duty. This compares with 79 recommendations made in 2003. Dr Whittle also made **58 suggestions** on matters of good practice, which compares with 120 made in 2003.

1.5 Unlike 2003, when Dr Whittle recommended to the Inspectorate that enforcement action be considered for six identified breaches of regulatory duties, there was only one issue arising during the 2004 audits that might have resulted in enforcement action being recommended.

1.6 Dr Whittle also made **26 recommendations to DWI** on follow up actions to be taken with specific companies. This compares with 13 made following the 2003 audits. He also made **six recommendations to DWI** arising from this summary report.

1.7 Dr Whittle considered that there had been an overall improvement since the 2003 audits, especially given the 17% increase in the number of samples audited. Furthermore a substantial number of the recommendations (19) were linked to deficiencies arising from the changes to sample scheduling and sampling under the new Regulations.

1.8 Many of the recommendations and suggestions were specific to the individual company, but there were a number of recurrent deficiencies. This report summarises Dr Whittle's main findings and includes a short review of the various analytical methods and their method performance. Good points are not specifically detailed but Dr Whittle found record keeping and the provision of information to be generally very good. He considered this to be an improvement on 2003 audits.

1.9 Dr Whittle visited almost all the laboratories undertaking potable water analysis on behalf of statutory water companies in England and Wales, as part of the audit process. He felt privileged to do so, and would like to thank the laboratories and their staff, as well as the water quality representatives, for their help and hospitality, and for the many stimulating discussions. A common theme arising from these visits was the requests for guidance and a desire to discuss topical issues. Dr Whittle found that the provision of sound technical guidance by DWI is much appreciated by the industry. He noted that during the last year in particular there has been the opportunity for companies to comment on draft guidance. He considered that the interest and lively discussion generated by these documents can only be beneficial. Dr Whittle trusts that this, his third audit summary report, will also prove informative and helpful.

2 Overall Conclusions

2.1 Dr Whittle concluded that:

- The presentation of the audit data was generally excellent. He much appreciated the hard work that went into sectioning the information and providing annotation of the relevant detail. However a number of companies did not follow the request for information fully, especially in terms of submitting a full record of the sampling round and full details of the public record entry for the sample.

- A number of companies experienced significant problems with sample scheduling and regularity of sampling following the introduction of the new regulatory regimes at the beginning of 2004. This also impacted on the analysis of samples, with problems in communicating analytical suites to or from contract laboratories.

- In general the standard of analysis had improved since 2003, although there were still areas for concern. The improvement in data presentation was much appreciated.

- The use of de-ionised water as the matrix for AQC samples was not generally appropriate, although necessary in a few instances.

- Although there had been improvements in quality control for residual chlorine measurements, eight companies were still not practising any form of regular quality control at the time of their audits.

- The analysis of isoproturon, chlortoluron and benzene was generally of a high standard.

- Given that lead has received much attention in recent years, the findings in respect of scheduling, analysis and, in some cases, the follow-up to failures, were disappointing. The levels of lead in the blanks used by some laboratories were also a cause for concern.

- The analysis of hydrogen ion was well done in some laboratories, but the general impression was that the parameter was not treated with sufficient respect. Sample stability was of concern and this issue also applied to other parameters.

- Reporting was largely satisfactory, with the number of significant figures reported being the main deficiency. There were a few issues relating to the new Regulations, particularly in respect of incorrect reporting (or analysis) of cyanide.

- The requirements of Regulation 17(6)(a) were not always satisfied fully in respect of notifying customers of lead failure attributable to the domestic

plumbing. Likewise the DWI guidance on the new Regulations was not always followed fully in respect of re-sampling after lead failures.

3 Recurring issues that resulted in recommendations and suggestions to the industry

3.1 Implementation of the new Regulations

3.1.1 Dr Whittle found that the approach to the implementation of the new Regulations was variable and, in some cases, disappointing. Some companies monitored the introduction of the new schedules very carefully, identifying problems at an early stage. Others tried this approach but were thwarted by flaws in their systems, which lulled them into a false sense of security.

3.1.2 Apart from regularity of sampling, which is dealt with below, there were serious deficiencies in scheduling the correct parameters. In some instances this was due to poor co-ordination with the analysing laboratory, where the wrong suites were scheduled. In other cases new requirements arising from the Regulations were simply overlooked.

3.1.3 Lead, benzene and cyanide were particularly problematic. Dr Whittle found that it took up to 6 months for some scheduling deficiencies to be identified, and one company completed almost a full year of cyanide determinations before it was made aware that the parameter had changed from free to total cyanide.

3.2 Regularity of scheduling and sampling

3.2.1 Regularity of scheduling and sampling was a major issue arising from the audits, with almost all companies failing to satisfy the requirements of Regulation 9 (4) to some degree. Dr Whittle accepted that all parties were on a learning curve at the beginning of the year but he made 19 recommendations. Most of these related to more than one parameter.

3.2.2 Dr Whittle found that many companies' scheduling procedures were based on a random sampling algorithm, which reduced regularity in a number of instances. This was particularly evident for lower frequency parameters at eight or less samples per annum. Dr Whittle accepted that the meaning of sampling at regular intervals is not defined in the Regulations. However the Interim Guidance states that 'It is important that there is a good spread between the sampling events.' He therefore adopted what he believed to be a reasonably generous tolerance, namely, that samples should be taken within +/- 25% of the target date. On that basis two consecutive samples should not be taken closer than half the sampling interval or apart by one and a half times that interval, where the interval was 366 divided by the number of samples scheduled for the year. He commented on what he considered to be a single minor infringement in the scheduling, but made a recommendation for multiple or more serious deviations.

3.2.3 Dr Whittle noted a number of occasions where regularity of sampling was affected by the analysing laboratory failing to notify the company as soon as maybe of AQC or other failures. He also found that feed back from contract laboratories to companies was poor in a number of instances. This was not so much in respect of broken or missing bottles, but more about failure to complete an analysis due to AQC failures or instrument breakdown.

3.2.4 Dr Whittle also noted that a number of companies omitted to amend their sampling schedules to take account of 1 January 2004 falling mid-week. This resulted in a number of 2004 samples being scheduled and taken during the final days of 2003. Given that this part of the new Regulations did not commence until 1 January 2004, these samples had to re-scheduled as soon as the problem was realised.

3.3 Over-sampling

3.3.1 Dr Whittle found that a number of companies still tended to over schedule for parameters such as residual chlorine, hydrogen ion and lead. He accepts that the Regulations specify the minimum number of samples to be taken. He also accepts that some companies have a policy of analysing each sample for a number of parameters over and above the regulatory requirements. However he considers that a clear distinction needs to be made in the purpose codes between compliance and operational samples, including any special survey samples e.g. for plumbosolvency control.

3.4 Sampling in general

3.4.1 Dr Whittle considered samplers' records to be generally good. However there were a number of problems on record keeping in respect of traceability of comparator discs, photometers and pH meters (for field analysis).

3.4.2 Dr Whittle also noted a number of instances of inadequate chain of custody records, especially where couriers were used to collect and deliver samples from drop off points. He considers that chain of custody is particularly relevant when samples are not logged in at the laboratory on the day of sampling. It should be possible to identify where a sample is stored and under what conditions at all stages between the sample being taken and the start of analysis.

3.5 Time between sampling and analysis

3.5.1 Dr Whittle found sample storage to be an ongoing problem from 2003. He reminds the industry of the draft guidance that DWI has recently issued on stability testing, and of the guidance available in ISO 5667 Part 3:2003.

3.5.2 He looked at stability and storage times for hydrogen ion analysis as part of his 2003 audit. This parameter was again selected for 2004 and Dr Whittle commented specifically on differing practices that remain ongoing.

3.5.3 ISO 5667 Part 3:2003 recommends a maximum storage time prior to analysis for hydrogen ion of just 6 hours. Of the 15 companies were audited for hydrogen ion, three carried out field measurements. Dr Whittle found that only three of the other companies specified maximum storage times in their methods and these ranged from 1 to 4 days. Most of the companies that did not specify a storage time were operating systems that analysed the sample on the day of receipt or within 24 hours. However no allowance was made for instrument breakdowns or public holidays. Furthermore a number of companies undertook both field and laboratory measurements for hydrogen ion, often on the same sample. Dr Whittle did not ascertain whether this was due to the nature of the sample, or to other operational requirements. He considers this worthy of further investigation in the future.

3.6 Analytical Quality Control

3.6.1 Dr Whittle considered that analytical control charts had generally improved. He found that a number of companies had benefited from increasing the number of points used in recalculations, while still reviewing charts at 60-100 points.

3.6.2 He noted that some laboratories were using fixed control limits on control charts and he deemed this to be unacceptable on three counts. Firstly, when used as temporary limits until sufficient data has been collected to calculate statistical limits. This usually occurs when a new control value is introduced or there has been an instrumental change (e.g. the installation of a new detector installed). The use of fixed limits in this situation shows that there has no been a proper assessment of the change. Sufficient testing needs to be undertaken to establish new limits. Where a new control limit is adopted, it is reasonable to expect the laboratory to undertake the testing and to establish the control limits prior to implementation. In situations involving instrumental change, it may be sufficient to establish a new mean and apply the current relative standard deviation. Secondly, some laboratories may cap limits at the target standard deviation (e.g. 5% target, warning limits at $\pm$10%, action limits at $\pm$15%). This is likely to occur when a method is not performing quite as well as it should and the laboratory accepts an increased number of failure situations. This would imply that the method performance has deteriorated from its validated position. The control chart should be reviewed and the problem investigated. Corrective action may have to include re-validation. Thirdly, situations arise where the performance of a certain method is very good (e.g. less than 1.5% relative standard deviation) and limits are capped at a 'workable' level. When limits become too tight, resulting in a high proportion of failures, then the number of points included in recalculations is possibly insufficient. Associated with this situation, and also where the standard deviation is well within the target value (but not capped), is the occasional belief that if an AQC result is outside the action limits, but within the target, then the associated results are acceptable. This concept is not acceptable given that NS30 states that the results associated with AQC failures are probably in error.

3.6.3 Dr Whittle found that a number of data systems used for control charts apply the current limits to all the data displayed. This makes it difficult to audit charts

prior to the last recalculation, and to assess the effectiveness of the control limits. He suggested that laboratories with such systems should maintain paper copies of the charts as used, and ensure that the specification for any future replacement system eliminates the problem.

3.6.4 Dr Whittle also discovered that, when significance testing of current AQC performance against previous performance was carried out, a decision that the performance was not significantly different could result in the new limits continuing to be inappropriate if previous limits were inappropriate.

3.6.5 Dr Whittle considered that where possible the matrix used for control samples should reflect the samples being analysed. He accepts that for some parameters the use of deionised water is the only practical option. He also accepts that it is not usually practical to undertake AQC using all the water types analysed but, where feasible, laboratories should be encouraged to use real matrices for a wide range of parameters.

3.6.6 Finally, Dr Whittle was concerned to find that in a small number of instances the fundamental principles of analytical quality control were still being ignored. These included the use of fixed control limits as discussed above (and not just for residual chlorine or hydrogen ion), failure to investigate step changes in control charts and acceptance of associated results, regular positioning of a control sample immediately after calibration standards leading to a slightly biased data set, and inadequate treatment of blanks.

3.7 Proficiency Testing

3.7.1 Dr Whittle was pleased to report that that in the main, proficiency-testing results were very good. He cited two examples, both relating to failures for benzene. In one case a thorough investigation was carried out, which highlighted instability of internal standards, and corrective action was taken. The investigations were well documented and more recent distributions gave good results. In the second case, the cause of the failure was assumed rather than being investigated fully. Although the basic technique was appropriate, the application was not. The information from the proficiency testing provided additional evidence for Dr Whittle to conclude that the method was not fit for purpose.

3.7.2 One aspect of proficiency testing that Dr Whittle considered should be regularised relates to the use of multiple instruments for a particular method or parameter. He found that some of the larger laboratories could be using two, three or even four instruments for analysing the same parameter. Satisfactory performance in external proficiency testing schemes should be demonstrated for all instruments used for compliance monitoring. Dr Whittle was advised by 'Aquacheck' that it was looking to change its systems to accommodate results from multiple instruments.

3.8 Other laboratory issues

3.8.1 Dr Whittle considered that when a company changes its analytical contractor, it should ensure that all necessary provisions for the satisfactory transport of samples (e.g. cooling and temperature recording, as necessary; chain of custody records) are in place, prior to the commencement of the contract.

3.8.2 Dr Whittle was disappointed to observe that many laboratories do not make best use of the expertise available within their own organisations. He also found that good practice was not always uniformly applied across all sections of a laboratory. He investigated a number of serious deficiencies or malpractices during 2004, which reflected his findings in previous years. In all cases he considered that there were people in the laboratory or company with sufficient knowledge and expertise to have identified the problem before it became an issue. He strongly recommended that companies and laboratories should undertake more internal cross-auditing of methods. He considers that this should not be made into an onerous task, but the simple expedient of another experienced analyst reading and witnessing a method and looking at control charts and PT results. Any queries raised should initiate discussion and basic errors could be identified and remedied.

4 Specific recommendations to DWI

4.1 Dr Whittle recommended to DWI that:

- Residual chlorine be audited again, when companies have had sufficient time to implement the requirements of the DWI's 'Guidance on Calibration and Analytical Quality Control for residual Chlorine Measurements', issued in January 2005.

- Consideration should be given to issuing guidance on sample preparation for metals analysis. Furthermore a specialist in trace metals analysis should be asked follow up the concerns regarding high lead blanks.

- The analysis of hydrogen ion is worthy of further attention in the future, with particular emphasis on testing in relation to sample stability, and field-testing.

- Consideration should be given to issuing guidance on sample storage times and stability, which have been a re-occurring theme in the audits of the past three years.

- Consideration should be given to issuing guidance on choice of matrices for the purposes of AQC.

5 Method performance

5.1 Summary tables of the performance of individual laboratories are appended. Standard deviations and bias are generally estimates from the control charts and averaged over the timescale of the charts, and therefore represent current performance rather than that at validation. The analytical techniques listed in the summary tables were those used for the samples audited, and may not be the only technique used by the laboratory for that analysis.

5.2 Specific comments on method performance for individual parameters are provided below:

5.2.1 Residual Chlorine

Dr Whittle was pleased to report an overall improvement in the analytical quality control of residual chlorine measurements, with more companies practising regular quality control compared 2003. However it was still disappointing that eight out of the 26 companies were not practising AQC, although two planned to introduce regular AQC after the audit.
At the end of January 2005 DWI issued guidance on calibration and quality control for residual chlorine measurements. This guidance was particularly helpful in clarifying the distinction between calibration checks and quality control. The guidance also suggested a range of options for quality control to enable companies to select an option appropriate to their own circumstances.
The audits showed that the use of control charts, or other effective means of statistical evaluation and control and review, was still poor. However Dr Whittle was pleased to record that several companies were proactive in developing innovative approaches to AQC. He particularly commended the two companies using control charts based on Z-scores.

5.2.2 Isoproturon/Chlortoluron

These analyses were well performed, with only 11 recommendations (and 11 suggestions) arising from the samples audited. Dr Whittle found that LC-MS is becoming increasingly popular with six out of 15 laboratories using the technique. Seven laboratories used UV diode array detectors. Bias was generally small and relative standard deviations ranged from 1.9 to 7.0%.
The recommendations were mainly in respect of scheduling, but there were several relating to maximum storage time or not analysing the sample within the specified time scale.

5.2.3 Lead

Given that lead has received considerable attention over the past few years, Dr Whittle considered that the analysis was not well done. The audits resulted in 22 recommendations and 10 suggestions, many of which were due to companies not adequately addressing the requirements of the new Regulations. Regularity and over-sampling have already been discussed, but the audits also revealed a

lack of standards below the pcv; inappropriate control standards; delays in implementing new control limits; and failure to analyse a first draw sample.

Dr Whittle also found considerable variation in sample pre-treatment between laboratories, with several laboratories using an oven digestion procedure. Others just allowed the acidified sample to stand for a given time. There was some evidence that this latter process may not be sufficient for samples containing particulate lead.

Dr Whittle noted that one company recorded a high blank value of almost 1 µg/l. This led him to look further at blank values and policies on blank correction. A summary of his findings are included in the lead section in the Appendix.

The variable number of results for each company reflects in part the number of lead samples audited, but also the way each laboratory works. Some laboratories always run a blank as part of the calibration and automatically blank correct all results. There may only be one, or in some instances no independent blank in the run. In some instances Dr Whittle has therefore calculated the blank value from the signal in relation to the top standard to give an approximate value. Other laboratories run a series of independent blanks and, depending on the values, decides whether to correct or not. The ICP-MS data show blanks ranging from –0.75 to 1.04 µg/l.

The use of blank corrections needs to be considered in terms of the prescribed concentration or value of the parameter being analysed. Where the blank result is as high as 4% of the current pcv (and 10% of the future pcv), correcting for the blank could have a significant impact on results close to the pcv. Dr Whittle would like to urge companies and contract laboratories to pay particular attention to blank results for lead. Values should be monitored, so that any instrumental problems can be identified, and an appropriate blank correction policy should be applied. He would also like to remind laboratories that the statistical limit should be used when decisions or comparisons are made in relation to the limit of detection, not a rounded up reporting limit.

5.2.4 Benzene

Given that benzene is a new regulatory parameter, Dr Whittle was pleased to report that the majority of laboratories had achieved an excellent standard of analysis and performance. He considered the analytical method unfit for purpose at only two of the 14 laboratories audited. One laboratory was using flame ionisation detection, which had just enough sensitivity in clean samples, but lacked specificity, and more seriously, had an occasional interferent very close to benzene that would have masked amounts close to the limit of detection. The basic technique (purge and Trap GC-MS) was sound at the other laboratory, but the application was seriously flawed by preparation of intermediate standards in water and an ineffective measure of system suitability.

Five laboratories used purge and trap and the other nine used headspace. Relative standard deviations ranged from about 3 to 8%, and bias typically –5 to 7%. Three laboratories did not specify a maximum storage time. Where specified storage times ranged from 7 to 20 days. There was a total of 18 recommendations and 5 suggestions arising from the 34 samples audited.

5.2.5 Hydrogen Ion

Although Dr Whittle did not consider his 15 recommendations and four suggestions excessive, he concluded that the analysis of hydrogen ion was possibly not given the attention that it deserved. Three companies measured hydrogen ion on-site. The remaining 12 companies used laboratory analysis and eight did not specify a maximum storage time in the methods. Dr Whittle accepted that most companies undertake the analysis to a tight schedule, the process can break down at public holidays or as a result of instrument break down. A number of the recommendations therefore related to timescale of analysis/stability, system suitability, inappropriate control limits, inadequate documentation and contingency plans. Dr Whittle also noted that in some cases both field and laboratory tests were carries out and he had concerns where there was a difference between the results.

APPENDIX 1

SUMMARY TABLE OF METHOD PERFORMANCE

Residual Chlorine – Photometers

Calibration Check Frequency	Quality Control	Comments
Daily	Daily at a fixed tap	Hach photometers
Daily	None, but monthly AQC planned	Hach photometers
Daily	Monthly blind samples based on permanganate, +/- 10% fixed limits	Hach Pocket Colorimeter
Daily	Monthly blind samples using chlorine solutions	Palintest 7000 photometers Control charts are plotted using Z scores to allow for varying concentrations
Daily	Weekly iodate solutions at 0.2 mg/l Cl	Hach Pocket Colorimeter A tabular chart is used with fixed limits of +/- 10%
Daily	Quarterly permanganate at 3 levels to be reduced to 6 monthly	Palintest 1000 or Hach Pocket Colorimeter
Primary cal. using iodine solutions, secondary cal. daily using gel standards.	None	Hach photometers AQC trial have been held
Daily	None	Hach Pocket Colorimeter
Daily	Weekly at a fixed tap	Hach Pocket Colorimeter
Daily	No regular AQC, occasional exercise	Palintest or Hach photometers
Daily	Monthly permanganate	Palintest 5000 & 1000 photometers. Very effective charts using z scores
Daily at 0.2 mg/l, monthly at 0.5 and 1.0 mg/l	Monthly using chlorine solution	Palintest Chlorometer Duo 1000 Control charts are plotted using Z scores to allow for varying concentrations, but fixed limits of +/- 20% used.
Certified solutions from Palintest, at 0.2 and 1.0 mg/l, are used for calibration of meters.	Weekly using certified solutions from Palintest, at 0.2 and 1.0 mg/l	Palintest Chlorometer 1000
Weekly for photometers, annually for comparators	None	Palintest 5000 & 7000 photometers and comparators are in use
Daily for photometers, annually for comparators	None	But monthly externally provided chlorine solution, +/- 20% fixed limits is being introduced
Monthly	Quarterly blind samples at 3 concentrations plus a blank	Palintest Chlorometer 1000 with comparators for back-up. Conventional control charts are not plotted, but the results for a group of samplers are plotted on a single chart allowing visual comparison of their relative performance.
Monthly	Quarterly blind samples at 3 concentrations plus a blank	Palintest Chlorometer 1000 with comparators for back-up. Conventional control charts are not plotted, but the results for a group of samplers are plotted on a single chart allowing visual comparison of their relative performance.

Monthly gel standards + twice yearly permanganate solutions	Daily at a fixed tap	Palintest 5000
Quarterly calibration and daily checks	None	Palintest Chlorometer 1000. No true AQC is practised. Checks are performed on a daily basis during the sampler's round, at 0.5 and 2.0 mg/l using certified standards, but these are in effect further calibration checks, and do not test the whole of the measurement procedure.

Residual Chlorine – Nesslerisers and Comparators

Calibration Check Frequency	Quality Control	Comments
Twice yearly	Duplicates	Duplicates are of little value with Nesslerisers. the company is considering using photometers.
Inspected every 6 months, re-placed if damaged or re-certified every 2 years	Weekly 0.3 mg/l equivalent iodate solution, 6 monthly check in range 0.2 - 0.9 mg/l.	Charts are not plotted, but results are tabulated for review purposes. The 6 monthly blind AQC checks, externally provided, function as a proficiency test.
Annually by manufacturer	Weekly at 0.1 and 0.3 mg/l	No charts and generous tolerances
Annually by manufacturer	Monthly permanganate at mid-point of each disc	Control limits set from performance data
Re-certification of disc by manufacturer every 2 years	Monthly iodate at 0.2 mg/l	If closest value is not 0.2 mg/l, then AQC fails

Chlortoluron

Calibration range µg/l	Nominal µg/l	RSD %	Bias %	Method	Max. storage Time (days)	Comments
0 - 0.2	0.1	2.6	-1.3	SPE, LC-MS	14	Agilent
0 - 0.25	0.1	4.1	-1.0	Automated on-line SPE, HPLC-DAD	14	Prospekt
0 - 0.3	0.1	4.1	-4.0	SPE, HPLC-DAD	NS	

Isoproturon

Calibration range µg/l	Nominal µg/l	RSD	Bias %	Method	Max. storage Time (days)	Comments
0 - 0.5	0.1	4.1	-2.6	SPE, LC-MS	14	To be replaced due to interference on atrazine. HP-MSD
0 - 1.0	0.1	2.4	-4.0	SPE, HPLC-UV	14	
0 - 0.4	0.1			SPE, HPLC-DAD	21	No performance data, unextracted standards used for AQC at time of sample. Extracted stds now used.
0 - 0.12	0.1	5.0	-3.9	SPE, HPLC-UV	14 Extr + 14 anal	
0 - 0.25	0.1	4.0	-2.0	Automated on-line SPE, HPLC-DAD	14	Prospekt
0 - 0.3	0.1	6.8	1.0	SPE, LC-MS	5 Extr+10 anal from receipt	
0 - 0.5	0.1	7.0	-2.3	SPE, HPLC-DAD	14	
0 - 0.3	0.1	3.6	-3.7	SPE, HPLC-UV & SPE, HPLC-DAD	NS	
0 - 0.3	0.1	3.2	-3.2	SPE, HPLC-DAD	7 Extr + 7 anal	limits probably too tight
0 - 0.5	0.1	2.5	1.0	SPE, HPLC-DAD	7 from sampling	Storage has been recently reduced from 20 days.
0 - 0.4	0.1	4.5	-1.0	SPE, LC-MS	NS	
0 - 0.3	0.1	4.0	-1.0	SPE, LC-MS	14 Extr+7 Anal	
0 - 0.125	0.1	4.5	10.0	SPE, LC-MS	NS	
0 - 0.2	0.1	3.5	0.2	SPE, LC-MS	14	
0 - 0.4	0.1	1.9	1.1	SPE, HPLC-DAD	NS	

Lead

Calibration range µg/l	Nominal µg/l	RSD %	Bias %	Method	Blank values	Comments
0 - 30	20.0	3.7	2.0	GF-AAS	0.09	
0 - 12	10.0	#	-3.3 to 2.0	ICP-MS	0.007, -0.01, 0.009, 0.001, 0.005, 0.003, 0.012, 0.03	PE Elan 6100. # Mean & range charts.
0 – 50	25.0	2.2	-2.0	ICP-MS	0.029, 0.070, 0.061	PE Elan 9000
0 - 50	25.0	1.9	-2.4	ICP-MS	0.05, 0.05	PE Elan 6010. Also AQC at 50
0 – 50	5.0	4.0	0.6	ICP-MS	-0.033, -0.014	PE Elan 6000. Also AQC at 40 µg/l
0 – 60	25.0	1.6	0.8	ICP-MS	0.04, 0.18, 0.05	PE Elan 6100
0 - 100	25.0	3.0	1.0	ICP-MS	0.09	PE Elan 6000.
0 - 100	25.0	4.0	-2.0	ICP-MS	No data	PE Elan 6000
0 - 100	25.0	3.0	1.2	ICP-MS	0.011, 0.007, 0.01	PE Elan 6000
0 – 200	25.0	4.5	0.4	ICP-MS	No data	PE Elan 6100
0 - 100	25.0	3.2	ND	ICP-MS	-0.09, -0.15, -0.28, -0.19, -0.19, 0.2	HP4500. New chart not yet recalculated. Also AQC at 50 & 90 µg/l.
0 - 500	10.0	3.5	3.3	ICP-MS	-0.75, -0.71, -0.26, 0.3, -0.74, -0.11. -0.08, -0.61, -0.05, 0.89	HP4500 Plus
0 - 50	25.0	6.3	-4.0	ICP-MS	0.52, 0.42, 0.49, 0.09, 0.13, 0.39	Agilent 7500
0 - 60	15.0	1.7	-0.7	ICP-MS	0.20, 0.033, 0.10	Agilent 7500, also AQC at 50 µg/l
0 - 100	25.0	4.3	2.2	ICP-MS	1.04, 0.92, 0.52, 0.97, -0.76, 0.08, 0.52, 0.85	ICP-MS Agilent 7500
0 - 500	25.0	2.5	-5.6	ICP-MS	- 0.6, 0.0, 0.0	Plasmaquad 3
0 - 1000	25.0	4.3	3.4	ICP-OES	-1.88, 2.99,	Thermo Jarrell Ash ICAP 61E. Planning to change to ICP-MS

Note: The variable number of blanks for each company reflects in part the number of lead samples audited, but also the way each laboratory works. No data does not mean that blanks were not analysed.

Benzene

Calibration range µg/l	Nominal µg/l	RSD	Bias %	Method	Max. storage Time (days)	Comments
0 - 1.4	1.0	3.5	16.0	Purge & Trap GC-MS	14	
0 - 2.0	2.0	6.9	1.0	Purge & Trap GC-MS	NS	Limits capped at 5%
0 - 5.0	0.9	3.4	0.0	Purge & Trap GC-MS	14	
0 - 5.0	1.0	8.0	-5.0	Purge & Trap GC-MS	7	
0 - 10	1.0	2.5	-1.5	Purge & Trap GC-MS	14	limits probably too tight
0 - 2.0	1.0	7.8	7.0	Headspace, GC-MS	10 working days	
0 - 2.0	0.9	5.3	-4.4	Headspace, GC-MS	7	
0 - 2.0	0.9	4.4	4.4	Headspace, GC-MS	14	
0 - 3.789	1.0	5.1	-2.1	Headspace, GC-FID	NS	Considered not fit for purpose
0 - 4.37	1.0	5.1	0.1	Headspace, GC-MS	NS	
0 - 5	3.0	5.4 - 8.6	4.0	Headspace, GC-MS	14	
0 - 10	1.0	6.0	5.0	Headspace, GC-MS	20	
0 - 20	0.8	8.5	2.5	Headspace, GC-MS	7 from receipt	limits probably too slack
0 - 20	0.8	8.5	2.5	Headspace, GC-MS	7 from receipt	limits probably too slack

Hydrogen Ion

Calibration range	AQC Nominal	Std. Dev	Bias	Method	Max. storage Time	Comments
pH units					(days)	
Field tests						
4.0, 7.0 & 10.0	8.00	ND	ND	Manual, WTW meter	N/A	Field Test. Single fixed limits of +/- 0.14 pH units, probably equivalent to about 3 sd
7.0 & 10.0	None			Manual, Hanna pHep meter	N/A	Field Test Operating range not specified
7.0 & 10.0	9.23	0.04	-0.05 to 0.05	Manual	N/A	Field Test Low ionic strength buffer for AQC
Laboratory analysis						
4.0, 7.0 & 10.0	7.62	0.03	0.02	Manual	NS	Low ionic strength buffer for AQC
7.0 & 10.0	8.00	0.02	0.01	Manual, Radiometer PHM93	NS	
4.0 & 10.0	7.00	0.006	0.017	Radiometer SAC90	NS	
4.0 & 9.22	8.00	0.03	-0.11	Manual	NS	
7.0 & 10.0 Linearity checks at 4.0 & 11.0	8.00	0.03	0.00	Manual	NS	Fixed limits based on a standard deviation of 0.05 pH units, but in reality the standard deviation is typically 0.02 - 0.04 pH units.
4.0, 7.0 & 10.0	6.87	0.02	0.02	Anachem Autotitrator	3	Operating range 0 - 14
4.0, 7.0 & 10.0	8.00	0.02	0.03	Anachem Analyser	1	
4.0, 7.0 & 10.0	4.00 6.96 9.00	0.017 0.015 0.020	0.023 -0.010 0.057	Skalar robotic analyser	NS	
7.0 & 10.0	8.00	0.03	0.00	Skalar 100 robotic analyser	4	Operating range 6 - 10
4.0, 6.0, 8.0 & 10.0	9.22	0.025	-0.011	Peerless robot	NS	1 day turn round given, but no actual maximum storage time specified.
4.0, 7.0 & 10.0	8.00	0.04	-0.05	Peerless robot	NS	

NS = not specified N/A = not applicable