

VALIDATION DOCUMENT

ANALYSIS OF ARSENIC IN TISSUES BY

VAPOUR GENERATION ATOMIC

ABSORPTION SPECTROPHOTOMETRY

(SOP ACU/0289)

ANALYTICAL CHEMISTRY UNIT

Veterinary Laboratories Agency

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VAPOUR GENERATION ATOMIC
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VALIDATION DOCUMENT FOR THE ANALYSIS OF ARSENIC IN TISSUE BY VAPOUR GENERATION ATOMIC ABSORPTION SPECTROMETRY

SUMMARY

Arsenic (As) is extracted from 2 g sub-samples of tissue using wet acid (nitric, perchloric and sulphuric acid) digestion. The acid mixture allows for complete digestion of the tissue sample, including all fat tissue, and is applicable to all tissue types (kidney, liver or muscle) and all species tested (bovine, ovine, porcine, equine and avian).

The use of VGAAS gives analyte specificity via the formation of a volatile arsine hydride and measurement with a monochromatic light source produced from an arsenic hollow cathode lamp. Acid digestion produces in solution the two inorganic As(III) and As(V) forms of arsenic. Acidification with addition of potassium iodide is then utilised to reduce all As(V) to As(III). The formation of an As(V) hydride is inefficient (approximately 20%) whereas As(III) is 100%. Reduction of arsenic to the same form also keeps the chemical stoichiometry of the hydride formation correct. The hydride is formed upon reaction with sodium borohydride. VGAAS is a more sensitive technique for the analysis of arsenic in tissue than either ICP-AES or GF-AAS.

The Limit of Quantitation (LOQ) for the method is 0.05 mg kg^{-1} and the Limit of Detection $0.0003 \text{ mg kg}^{-1}$. The method has been tested with fortified samples and meets the accuracy requirements of 90/515/EEC. Precision data satisfies intra- and inter-batch variation predictions from the modified Horwitz Equation in incurred samples at three levels. A precision estimation has been set (in line with requirements of UKAS Document M3003) at $\pm 15\%$, equivalent to 2 standard deviations. The analyte has shown to be stable in matrix over several years. The method has been valid for application with bovine, ovine, porcine, equine and avian tissues.

VALIDATION DOCUMENT FOR THE ANALYSIS OF ARSENIC IN TISSUE BY VAPOUR GENERATION ATOMIC ABSORPTION SPECTROMETRY

1. INTRODUCTION

This document describes the validation of the method for the determination of residues of arsenic in bovine, ovine, porcine, equine and avian tissues. The procedure followed is that described in the Standard Operating Procedure ACU/0289 “The Determination of Arsenic in Tissue by Vapour Generation Atomic Absorption Spectrometry”. The flow diagram of the method is shown in figure 1.

The performance of the assay is examined and acceptance limits are set for operational use of the assay.

ABBREVIATIONS AND SYMBOLS

Abbreviation/Symbol	Definition
ACU	Analytical Chemistry Unit
SD	Standard deviation
CV(%)	Percentage coefficient of variance
r ²	Correlation coefficient
t	The ‘t’ statistical function
VG-AAS	Vapour Generation Atomic Absorption Spectrophotometry
CRM	Certified Reference Material
DI H ₂ O	Deionised Water
SOP	Standard Operating Procedure

2. CALIBRATION FUNCTION

A three point arsenic calibration curve is prepared at concentrations of 0, 2 and 4 ng cm⁻³ arsenic. The standards are matrix-matched to the extracted samples (8% sulphuric acid and 5% of a 20% potassium iodide solution and made up to volume with 1 M hydrochloric acid). The addition of KI under acidic conditions produces the

reduction of all As(V) to As(III) which more readily forms a volatile hydride.

Solutions are left for an hour before assaying to allow the reduction of all As(V) to As(III).

Figure 1. Flow diagram Determination of Arsenic in Tissue by VG-AAS (ACU 289).

**WET ACID
DIGESTION**

1. Weigh 1 g tissue into a digestion vessel.
2. Add 10 cm³ HNO₃ followed by 4 cm³ of 1: H₂SO₄:HClO₄.
3. Digest samples on hot block.

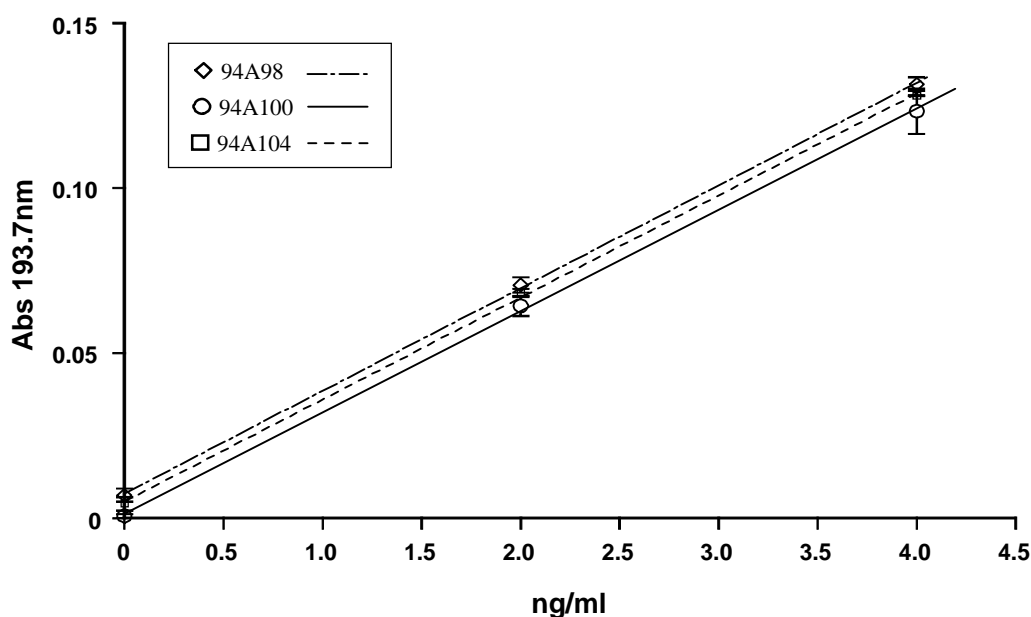
**VGAAS
PREPARATION**

1. Cool samples.
2. Rinse each vessel with 1 M HCl.
3. Transfer to a 50 cm³ polypropylene centrifuge tube.
4. Rinse digestion vessels and transfer to centrifuge tube.
5. Repeat step 4..
6. Make up to approximately 20 cm³ with 1 M HCl.
7. Add 1.25 cm³ of 20% KI and make up to 25 cm³ with 1M HCl.
8. Wait 1 hour before analysing.

VGAAS

1. Analyse by VGAAS.

Figure 2. Arsenic (As) calibration curves calculated from three separate assays [1].

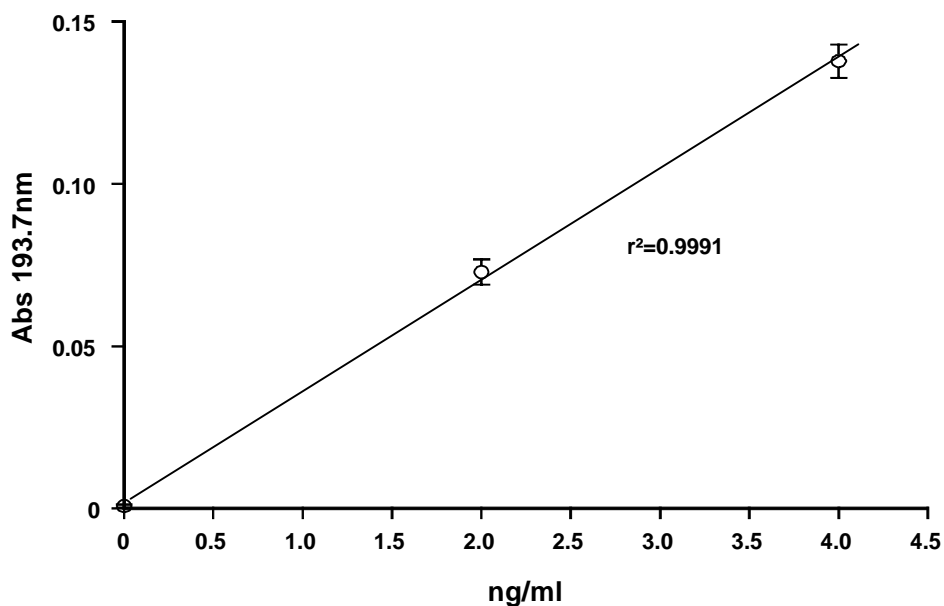


Calibration	Slope	Intercept	Correlation (r ²)
94A98	0.0315	0.007333	0.99996
94A100	0.03075	0.001167	0.9995
94A104	0.0347	0.000833	0.9996

For a detailed discussion of the calibration profile and variation with wavelength see section 9.2.

3. MATRIX FUNCTION

Negative control turkey livers were fortified in triplicate at the post-extraction stage of the assay, at levels of 0.050 mg kg⁻¹ and 0.100 mg kg⁻¹ (equivalent to the 2 ng cm⁻³ and 4 ng cm⁻³ standards used to produce the calibration curve). Figure 3 shows the matrix standard curve calculated from the means of the fortification results, with the 'error bars' representing the 95% confidence limit. The results of fortified tissue samples calculated against the matrix curve are given in Table 1.

Figure 3. Matrix standard curve.**Table 1. Matrix effects on fortified turkey liver, calculated on a three point calibration curve.**

Fortified level (ng cm ⁻³)	Result (ng cm ⁻³)	Recovery (%)
2.00	1.90	95
2.00	2.00	100
4.00	3.90	98
4.00	3.80	95
4.00	3.60	90
4.00	4.00	100

4. PRECISION

This is defined as the inter- and intra-batch variation of the results for QC materials taken through the assay. Two “in-house” QC materials containing arsenic were produced; the first (QC09) fortified to approximately 0.100 mg kg⁻¹ and a second (QC10) fortified to approximately 0.350 mg kg⁻¹. Each QC material was assayed to establish the intra-batch variation (replicates in the same digest), shown in Table 2, and inter-batch variation (separate digests of the QC material), shown in Table 3. The results were compared to the variation, as %CV, calculated from the modified Horwitz Equation. The acceptable precision for any analytical result from the assay is set as two standard deviations, i.e. the

95% certainty level. The experimental data presented in Tables 2 and 3 indicate this to be $\pm 20\%$.

Table 2. Intra-batch Variation

Assay no.	93A196	93A197	93A196	94A2
QC09				
mean	0.094 mg kg ⁻¹	0.098 mg kg ⁻¹	0.104 mg kg ⁻¹	0.108 mg kg ⁻¹
n	7	14	6	6
SD	0.006	0.008	0.004	0.007
%CV	6	8	3	7
Horwitz %CV	23	23	23	23
QC10				
mean	0.334 mg kg ⁻¹	0.367 mg kg ⁻¹	0.359 mg kg ⁻¹	0.398 mg kg ⁻¹
n	6	12	8	6
SD	0.008	0.028	0.014	0.016
%CV	3	8	4	4
Horwitz %CV	19	19	19	19

Table 3. Inter-batch Variation.

	QC09	QC10
mean	0.098 mg kg ⁻¹	0.367 mg kg ⁻¹
SD	0.008	0.028
%CV	8	8
Horwitz %CV	23	19
n	37	37

5. ACCURACY

Accuracy is expressed using recovery data from incurred and certified Reference Materials. The documented EC limit for accuracy is $\pm 10\%$ [3]. Selected Certified Reference Materials (CRMs) BCR186 [4] and NBS1577a [5] were analysed.

Fortified avian samples were analysed and checked for accuracy. Samples were fortified at 0.050, 0.100 and 0.500 mg kg⁻¹. These extracts contained 1 g of digested wet tissue. The results in Table 5 indicate a high level of accuracy for fortified tissues and are all within the precision limits set for the data $\pm 15\%$.

Table 4. Recovery of arsenic from Certified Reference Materials

	BCR186	NBS1577a
certified level (mg kg ⁻¹)	0.063	0.047 mg kg ⁻¹
mean recovery (mg kg ⁻¹)	0.044	0.039 mg kg ⁻¹
recovery %	70%	83%
range of results (mg kg ⁻¹)	0.035-0.061	0.032-0.048
n	9	9

Table 5. Accuracy of extracted fortified avian livers.

fortified level (mg kg ⁻¹)	n	results (mg kg⁻¹)	mean recovery (%)
0.050	6	0.048, 0.053, 0.055 (2), 0.058 (2)	109
0.100	9	0.088, 0.093 (2), 0.094, 0.100 (2), 0.103, 0.108 (2)	99
0.500	6	0.500 (3), 0.513 (3)	102

Due to the low levels of arsenic in the CRMs, 1g of dry powder (equivalent to 5 g of wet tissue) was analysed. The extraction procedure appeared to be capable of fully digesting this amount of material, producing clear digests. However due to the arsenic levels being close to the method's limit of quantitation (see section 8), the large levels of matrix present in the extract may have had a detrimental effect on the results, giving low recoveries.

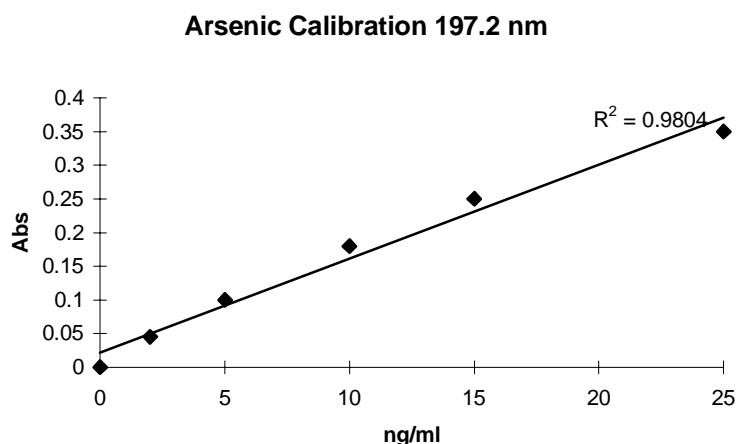
6. SENSITIVITY

Sensitivity is defined as the slope (response/concentration) of the calibration curve [3]. Table 6 describes the sensitivities of the calibration curves from Figure 1.

Figure 4 shows that the calibration has a quadratic function which the Varian software can calculate, however standard curves up to 4 ng cm⁻³ show linearity to three decimal places.

Table 6. Sensitivity of this assay for arsenic

	1	2	3
Slope (A ng⁻¹ cm⁻³)	0.0316	0.0305	0.0347
Intercept (A)	0.007333	0.001167	0.000833

Figure 4. Calibration linearity at the 197.2 nm wavelength

7. SELECTIVITY

Hydride generation procedures experience some degree of interference in the presence of transition metals. Nickel is known to interfere with the determination of arsenic by atomic absorption spectrophotometry [6]. The results, summarised in Table 7, show that standards containing 2 ng cm⁻³ and 4 ng cm⁻³ of arsenic and fortified with 100 ppm nickel exhibit absorbance readings comparable to standards at similar levels without nickel [7]. Results for blank tissue fortified with arsenic prior to acid digestion gave results within acceptable limits, irrespective of nickel concentration [8]. These are summarised in Table 8.

The results in Table 7 show that 2 ng cm⁻³ arsenic standards containing 100 ppm nickel were 2% lower; and the 4 ng cm⁻³ arsenic standards containing 100 ppm nickel were 4% lower than analytical standards. Use of a statistical t-test establishes that there is no significant difference between the 2 ng cm⁻³ arsenic standards that contain 100 ppm nickel and those that do not. However, there is a significant difference between the results (t-calculated in Table 7 below) for the 4

ng cm⁻³ arsenic standard containing no nickel and 100 ppm nickel at the 95% probability level (t-critical). This concentration of nickel is well in excess of that normally found in tissues.

Table 7. Effect of nickel on arsenic standards.

	2ng cm ⁻³ As std	2ng cm ⁻³ As std + 100 ppm Ni	4ng cm ⁻³ As std	4ng cm ⁻³ As std + 100 ppm Ni
i	1.90	1.80	3.90	3.70
ii	2.00	2.00	4.10	3.90
iii	2.00	2.00	4.20	4.00
iv	2.00	2.00	4.10	3.90
v	2.00	1.90	4.00	3.90
Mean	1.98	1.94	4.06	3.88
t-calc	0.0568		2.41	
t-crit	2.31		2.31	

Table 8. The effect of nickel on tissue fortified with arsenic.

	Arsenic spike (mg kg ⁻¹)	Nickel content (ppm)	Recovery
i	0.050	0	100%
ii	0.050	100	95%
iii	0.100	0	90%
iv	0.100	25	95%
v	0.100	50	100%
vi	0.100	100	98%

8. LIMIT OF QUANTITATION

Blank avian livers were fortified in duplicate from 0.010 mg kg⁻¹ to 0.050 mg kg⁻¹ in 5 mg intervals. Three separate digests [9] were assayed. A summary of the results are presented in Table 9.

From this data it is deduced that arsenic fortification levels below 0.035 mg kg⁻¹ (35 ng g⁻¹) show a low degree of precision. The precision limit decided (see Section 4) for analytical quantitation based on the experimental evidence was two standard deviations, i.e. ± 15. The method's limit of quantitation is thus 0.035 mg kg⁻¹. However, the precision of the fourth significant figure, i.e. at the

0.001 mg kg⁻¹ level, is questionable. Thus, the limit of quantitation should be limited to three significant figures or the 0.01 mg kg⁻¹ level. Therefore the limit of quantitation is rounded up to 0.04 mg kg⁻¹. However, and in combination with the data above in Section 5 covering accuracy, most work has been done at the 0.050 mg kg⁻¹ level and it was decided to follow this and set the limit of quantitation at 0.05 mg kg⁻¹. This is still significantly lower than the prescribed MRL of 1.00 mg kg⁻¹.

Table 9. Blank avian livers fortified with a range of arsenic concentrations

Spike Conc. (mg kg⁻¹)	Mean Conc. Recovered (mg kg⁻¹)	Mean Recovery (%)	SD (n)	%CV	2SD as % of mean
0.010	0.009	88%	0.007 (6)	82%	165%
0.015	0.013	84%	0.008 (6)	63%	126%
0.020	0.018	88%	0.008 (6)	46%	93%
0.025	0.029	106%	0.005 (6)	19%	38%
0.030	0.032	107%	0.005 (6)	15%	30%
0.035	0.041	115%	0.002 (5)	5%	10%
0.040	0.046	115%	0.001 (6)	3%	6%
0.045	0.053	117%	0.002 (6)	4%	9%
0.050	0.058	116%	0.004 (6)	6%	13%

9. LIMIT OF DETECTION

Twenty analytical blanks went through the digestion procedure and were assayed [10]. Results are summarised below.

$$\text{Mean} = 0.09 \text{ ng cm}^{-3}$$

$$\text{SD} = 0.091$$

$$\text{Limit of detection} = 3 \times \text{SD (per mass of sample) [3]}$$

$$= 3 \times 0.091 \text{ ng cm}^{-3}$$

$$= 0.273 \text{ mg kg}^{-1}$$

$$= 0.0003 \text{ mg kg}^{-1}$$

10 ROBUSTNESS

10.1 Wet Acid Digestion

To digest 1g of wet tissue samples in 10 cm³ HNO₃ and 4 cm³ of 1:1 H₂SO₄:HClO₄ (v/v) the Tecator hot block temperature program in Table 10 is used. [2]

Table 10. Tecator hot block digestion program

	Temp	Ramp	Hold
Step 1	110°C	0.1 hours	1.0 hours
Step 2	160°C	0.1 hours	1.0 hours
Step 3	200°C	0.1 hours	3.0 hours

This procedure was able to completely digest 2g of all species and tissue types except horse liver which had a small amount of fat remaining. Equine tissue is currently not on the National plan.

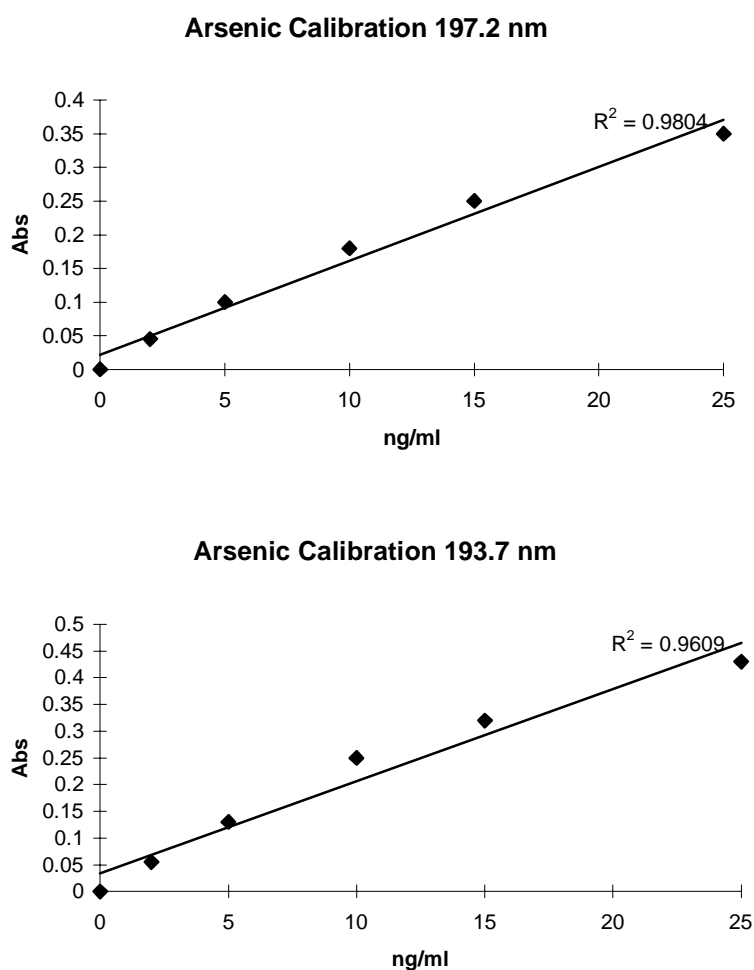
10.2 Wavelength

The current Standard Operating Procedure [2] uses the 193.7 nm spectral line, with standards at 2 ng cm⁻³ and 4 ng cm⁻³. An alternative is the 197.2 nm spectral line which has a greater linear working range (0-50 mg kg⁻¹) [11]. Calibrations at each spectral wavelength were carried out ranging over differing concentration ranges and linearity assessed by calculating the correlation coefficients (R²) for the calibration curves. (R² is the coefficient of determination and is a measure of the correlation between actual values and those determined from a calculated line of best fit. The R² value is a dimensionless number, the significance of which resides in the last non-9 digit. [12])

The results show that the Varian AAS software will always produce a quadratic curve. The linearity for a 0 to 10 ng cm⁻³ five point standard curve at both 193.7 nm and 197.2 nm is good with R² values of 0.993 to 0.999 for 193.7 nm and 0.997 to 0.999 for 197.2 nm. Comparisons of the linearity of curves for the two wavelengths at arsenic concentrations greater than 10 ng cm⁻³ shows that the 193.7 nm spectral line begins to lose its linearity at lower concentrations than

the 197.2 nm (see figure 5). Since the 193.7 nm spectral line is documented as more sensitive[15] than the 197.3 nm spectral line and generally only low levels of arsenic are found in analytical samples, the decision was to use the more sensitive 193.7 nm spectral line.

Figure 5 Comparison between standard curves at 197.2 nm and 193.7 nm



10.3 Standards

Standards made following the instructions in Standard Operating Procedure ACU/289 are matrix matched to the samples and contain 8% H_2SO_4 in 1 M HCl. A comparison was made between these standards and those made up in just 1 M HCl [14]. This was assessed by producing a calibration curve with standards containing 8% H_2SO_4 in 1 M HCl and calculating the concentration of the standards made up in 1M HCl from the calibration curve. The results obtained showed a difference of less than 10 % throughout the calibration range.

However in consequent assays it has been noticed that standards made in 1 M HCl only show a greater degree of intra-assay variation in absorbance values [15]. Thus, the experimental data indicates that matrix matched standards give greater confidence in the analytical results.

10.4 Comparison of Acid Grade

A comparison of analytical blanks was made between digestions using the more expensive AristaR HCl and H₂SO₄, and lower grade AnalaR HCl and H₂SO₄ [11]. Table 11 details the results of 20 blanks digested using the different grades of acids.

Table 11. Comparison of analytical blanks digested with AristaR and AnalaR grade acids

	Mean	SD
AristaR HCl and H ₂ SO ₄	0.09 ng cm ⁻³	0.091
AnalaR HCl and H ₂ SO ₄	0.09 ng cm ⁻³	0.091

There is no difference in the arsenic content of the blanks digested using the lower AnalaR grade acids. Therefore this grade of acid is suitable to use in the analysis of tissue.

10.5 Source of Sodium Borohydride

Sodium borohydride reducing agent purchased from both BDH and FLUKA have been compared by assaying standard curves prepared using the reductant from both sources [16]. Figure 6 and Table 12 detail the results of this comparison. The calibration curves and the statistical analysis using the t-test indicates that there is no significant difference between the sodium borohydride supplied by either company.

Figure 6. Comparison of standard curves using different source of reductant

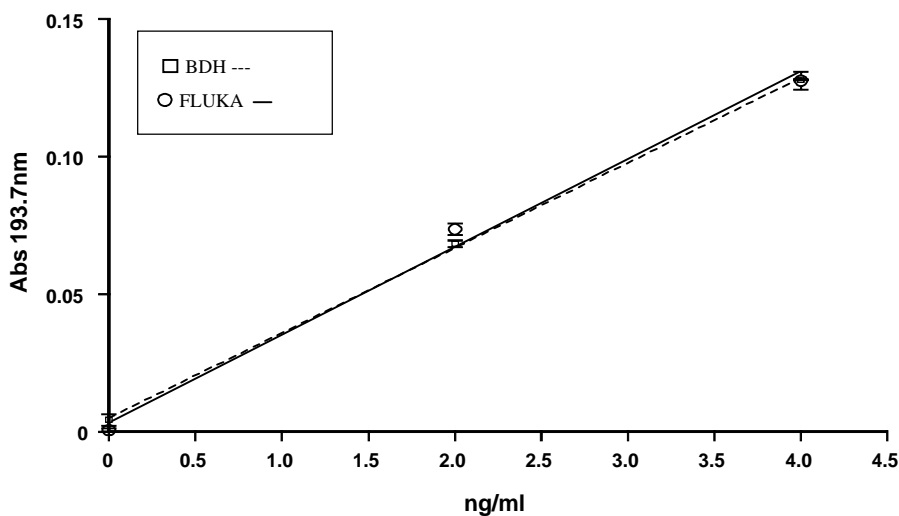


Table 12. Comparison of standard curves using different source of reductant

Standard Concentration	Absorbance	
	BDH	Fluka
0 ng cm ⁻³	0.003	0.005
2 ng cm ⁻³	0.065	0.068
4 ng cm ⁻³	0.123	0.129
t calc	2.618	
t crit	4.30	

10.6 Inter-species Comparisons

Ten fortified samples and five blank samples of liver and kidney for each species available were digested and assayed [17]. Tables 13 and 14 summarise the results obtained.

Analysis of variance (ANOVA) calculations have been performed to statistically compare these results[18]. Although the ANOVA calculations have shown that species are statistically different, all 50 results are within the $\pm 20\%$ precision limit set in Section 4 above and the accuracy of the results is good. Although there may be statistical differences between species, results are calculated on a standard curve and not a matrix curve. This has been shown to give accurate results. Batch QC would have eliminated any poor results. Any confirmatory

analysis must also be analysed in duplicate to ensure reproducibility.

Table 13. Recovery from liver fortified at 0.100 mg kg⁻¹

	Recovery (x 10 ⁻³ mg kg ⁻¹)										Mean
Turkey	93	88	118	113	108	108	93	88	83	108	100
Bovine	105	115	100	105	110	115	105	110	105	105	108
Porcine	88	90	95	100	100	105	90	90	100	90	96
Ovine	100	95	95	100	100	95	100	100	100	100	98
Equine	94	91	94	91	106	94	94	94	94	91	94
F _{4,45} calc	6.1										
F _{4,45} crit	2.69										

Table 14. Recovery from kidney fortified at 0.080 mg kg⁻¹

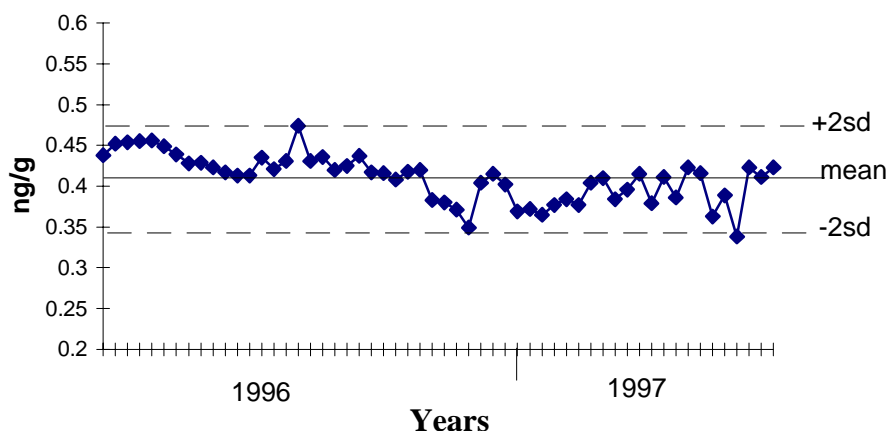
	Recovery (x 10 ⁻³ mg kg ⁻¹)										Mean
Bovine	85	78	78	83	78	75	78	78	83	83	80
Porcine	78	80	75	78	88	78	80	80	78	78	79
Ovine	88	73	75	80	80	75	80	85	78	80	79
Equine	78	75	78	78	78	75	73	78	75	80	77
F _{3,36} calc	1.7										
F _{3,36} crit	2.85										

ANOVA calculation indicate that there is no statistical difference between species when analysing kidney samples.

10.7 Analyte Stability

A fortified in-house prepared avian liver material (AsQC03) has been analysed over a period of two years to assess analyte stability in matrix. The data in figure 7 illustrates that the analyte is stable in matrix over a considerable length of time.

Figure 7. Analyte stability in matrix over time



An in-house prepared QC liver samples (AsQC02) was digested and assayed in the week after digestion [19]. Table 15 details the results obtained and shows that the extract is stable on the bench at room temperature for at least 6 days after extraction..

Table 15. Recovery data for In-house QC materials assayed in the week following digestion

Days from digest	AsQC02 (0.08 mg kg ⁻¹)	Recovery (%)
1	0.10	98
2	0.09	113
3	0.09	113
4	0.08	100
6	0.08	100

11. QUALITY ASSURANCE PLAN

11.1 Quality Control

Every batch of samples includes at least one appropriate in-house QC material, a fortified sample and at least two blanks. Every sample for confirmation must be run in duplicate.

Acceptance criteria	Action - if unacceptable
1. Recoveries of fortified material between 85 - 115% (2SD's).	Repeat the AAS stage of the analysis for the entire batch. If still outside limits, repeat the entire procedure.
2. % RSD for an individual sample $\leq 15\%$	Re-run the individual sample digest.
3. Duplicate samples differ by $\leq 15\%$ of their mean	Re-run the duplicate sample digests

The Analytical Chemistry Unit is a Good Laboratory Practice (GLP) accredited laboratory, hence all analysis are carried out to GLP standards.

Audits may be carried out at any time by the department of Health inspectors, Quality Assurance Unit auditors, or "peer" auditors from within the unit.

Copies of the audit report must be sent to the Chromatography/Spectroscopy Team Leader who must then:

- Identify and rectify any non - compliance highlighted.
- Respond as appropriate to the auditor.

All audit reports are stored by the Chromatography/Spectroscopy Team Leader.

11.2. External Quality Control Schemes

At this present time, the Analytical Chemistry Unit does not participate in any external quality control schemes for the analysis of arsenic in tissue.

12. REFERENCES

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