CHAPTER 4

THE QUANTITATIVE DETERMINATION OF MONO-ISOTOPIC ARSENIC IN ACIDIC MATRICES

4.1 Introduction

4.1.1 Aspects of the toxicity of arsenic

Inorganic arsenics have a toxicity rating reported to be 100 times higher than in organic forms *[53]*. The clinical manifestations of arsenic overdose are polymorphous, in particular, digestive, cardiovascular, neurologic, cutaneous and renal *[54 - 58]*. In the case of acute suicidal arsenic intoxication death can occur one week after digestion, despite intensive care *[59]*. The trivalent derivates are more toxic than the pentavalent forms and soluble forms (arsenites and arsenates) are more toxic than nonsoluble forms *[53]*. At cell level, arsenic toxicity is mainly due to an inhibition of enzymatic cell reactions, through an effect on the sulphydryl groups in enzymes *[59]*. Gradual increasing tolerance to arsenic appears to be significant *[59]*. Further effects of arsenic on the body are discussed in detail in literature *[59]*.

4.1.2 Levels of arsenic in the human body

Cutaneous absorption is low except in the case of damaged skin *[60]*. Arsenic accumulates mainly in hair, nails and teeth *[59]*. Elimination is both through the digestive and urinary systems *[54]*.

Normal arsenic values in hair (from 4.55 mg $(100\ g)^{-1}$ to 33.08 mg $(100\ g)^{-1}$ depending on the type of hair), normal arsenic values in various body parts (levels ranging from 0.002 mg dm^{-3} to 0.3 mg dm^{-3} depending on the topography), values in cases of acute intoxications (ranged from 0.7 ng g^{-1} in the brain to 654.0 ng g^{-1} in the stomach) are reported in references *[61, 62]*. Blood toxic levels are quoted as ≥ 1 mg dm^{-3} and lethal blood levels as ≥ 10 mg dm^{-3} *[63]*. Normal "unexposed" values for arsenic content as reported by some researchers *[64 - 66]* are < 2 mg dm^{-3} in hair and < 1.5 mg dm^{-3} in nails. Arsenic concentrations in blood of normal subjects range from 0.002 to 0.062 g dm^{-3} according to Heydorn *[67]*.

Although arsenic poisoning is usually associated with foul play, these elements may be consumed in connection with cultural and lifestyle preferences as showed in an examination of traditional Chinese medicines *[68]*. The arsenic content in the herbal balls varied from 0.1 mg to 36.6 mg per ball where the masses of the balls varied from 2.5 g to 9.0 g. The prescribed adult dose of two balls daily leads to a maximum elemental intake of 73.2 mg arsenic. Chronic and acute arsenic poisoning of 74 traditional Chinese medicine consumers in Singapore was reported in 1975 *[69]*.

4.1.3 Techniques employed

Several techniques are commonly employed for the qualitative and quantitative determination of arsenic. Some of these include: the Gutzeit method and the Reinsch Test *[70 - 73]*, silver diethylcarbamate colorimetric method *[74]*, radioactive methods *[75]*, XRF *[68]*, AAS *[68]*, GFAAS *[59]*, ICP-AES *[76]* and ICP-MS *[77 - 81]*.

After they compared results obtained by AA and ICP-MS, Tanaka *et al. [77]* concluded that the sensitivity of AAS for arsenic determination is inferior to that of ICP-MS. Other workers showed the advantages of ICP-MS as compared to ICP-AES for the determination of arsenic *[82]*.

4.2 Polyatomic ion interferences

4.2.1 Characteristics of polyatomic ions

Compared to elemental isobaric overlap, polyatomic or adduct ions cause more serious problems to ICP-MS analysis. In this form of spectroscopic interference the polyatomic ions result from the short-lived combination of two or more atomic species. Argon, hydrogen and oxygen are the dominant species in the plasma and they may combine with one another or with elements in the analyte matrix to form polyatomic ions. Although the composition of the gas extracted from the plasma at the interface is effectively frozen within approximately 1μs of leaving the plasma, fast ion molecule reactions can occur between species present in the gas. Although a large number of polyatomic ions can form, they are only significantly detected below 82 *m/z [83]*.

A number of authors *[29, 30, 34, 84 - 86]* have examined the factors affecting the formation of polyatomic ion interferences; these include: extraction geometry, operating parameters for plasma and nebuliser systems, specific instrument design and most importantly the acid and sample matrix.

The polyatomic ion peaks in both HNO_3 and H_2O_2 are identical to those identified in deionised water and these media are thus considered ideal matrices. Additional peaks are seen in the more complex spectra of HCl and H_2SO_4 matrices. Mono-isotopic arsenic has a mass of 75, the same mass as that at which the peak of the polyatomic ion $^{40}Ar^{35}Cl$ occurs.

4.2.2 *Possible procedures for the correction of polyatomic interferences*

Usually a correction may be made for the overlap of a polyatomic ion peak with an elemental peak, e.g. by using a reagent blank. However, these peaks may be relatively large compared to the analyte contribution at any given mass and a significant error may occur when a correction is applied *[83]*. In addition, polyatomic ion peaks are less stable than analyte ion peaks, introducing a further source of errors *[83]*.

Sakata and Kawabata *[84]* proposed the electrical decoupling of the plasma from the load coil (using a special device) and then changing the plasma conditions to attenuate ionisation of the polyatomic ions in order to effectively reduce the polyatomic ions. A high resolution ICP-MS was employed by Prohaska and co-workers and a separation of the peaks of $^{40}Ar^{35}Cl$ and As peak was obtained, that effectively rendered the As peak free from interference *[87]*. Some researchers *[78, 81]* used the $^{16}O^{35}Cl$ polyatomic ion to correct for chloride interference when determining As by means of ICP-MS. Other workers proposed a matrix matching technique which minimises differences in acidity and carbon loading in order to overcome the problem *[79]*. The addition of nitrogen to the aerosol carrier gas flow decreases the formation of the $^{40}Ar^{35}Cl$ polyatomic ion to negligible levels *[80, 88]*, but the nitrogen addition has the disadvantage of reducing analyte sensitivity *[89]*. Other workers developed a method of matrix elimination that facilitates determination of arsenic by means of ICP-MS without interference from polyatomic ions *[90]*. This method involves the retention of the analytes as anions on activated alumina (acidic form) in a microcolumn using an on-line flow injection system, with simultaneous matrix removal. Anderson and co-workers *[89]* suggested that hydride generation be employed as a means of eliminating chloride interferences while maintaining sufficient analyte sensitivity for the determination of arsenic by means of ICP-MS.

Since the problem of the $^{40}Ar^{35}Cl$ interference on ^{75}As is recognised by many ICP-MS users *[49, 91]*, many chose to work in a nitric acid matrix when determining arsenic *[49, 77, 82, 91]*.

4.3 Arsenic determinations in biological samples

Usually hair, nail and other biological samples are digested in nitric acid using a microwave method *[92 - 94]* and the resulting solutions can be used for ICP-MS determinations when very low levels of arsenic has to be determined. In the case of more indigestible inorganic samples hydrochloric acid also has to be employed in the sample preparation procedures. It is thus the aim of this work to investigate the determination of arsenic at $\mu g\ dm^{-3}$ levels in nitric acid and hydrochloric acid matrices. The effects of different correction procedures, similar to those proposed by Nixon, Lásztity and others *[81, 94]*, as well as internal standards on the quantitative determination of arsenic by ICP-MS will also be monitored.

The feasibility of using the following isotopes as internal standards in arsenic determination was investigated: ^{45}Sc, ^{89}Y, ^{139}La, ^{36}Ar, ^{35}Cl and ^{37}Cl. ^{45}Sc, ^{89}Y and ^{139}La were added to the solutions and ^{36}Ar, ^{35}Cl and ^{37}Cl were present due to the argon plasma and the nature of the matrices of the solutions. Table 4.1 shows the relevant data of arsenic and the internal standards investigated.

The determination of arsenic in the following acidic matrices were investigated: concentrations of HNO_3 ranging from 0.10% v/v to 2.50% v/v HNO_3, concentrations of HCl ranging from 0.10% v/v to 2.50% v/v, mixtures of HNO_3 and HCl with combined concentrations of 0.20% v/v to 2.00% v/v.

4.4 Experimental

4.4.1 Preparation of solutions

Table 4.2 shows the results of the calculations performed in order to prepare stock solutions of arsenic and the internal standards added. Table 4.3 shows the results of similar calculations for the preparation of arsenic calibration standards in 1.00% v/v HNO_3 and 20 $\mu g\ dm^{-3}$ arsenic samples in various acidic matrices. Arsenic calibration standards were prepared in the range from 0 to 100 $\mu g\ dm^{-3}$ and 20 $\mu g\ dm^{-3}$ arsenic sample solutions were prepared in matrices of 0.10% v/v to 2.50% v/v HNO_3 and HCl.

Table 4.1: Relevant data of arsenic and the internal standards investigated *[50]*.

Atomic no.	**Element**	**Mass no.**	**Relative abundance**	**Atomic mass ($g\ mol^{-1}$)**	**First ionisation potential (eV)**	**Second ionisation potential (eV)**
17	Chlorine	35 37	75.53 24.47	35.453	13.02	23.80
18	Argon	36 38 40	0.337 0.063 99.600	39.948	15.76	27.63
21	Scandium	45	100.0	44.956	6.56	12.80
33	Arsenic	75	100.0	74.922	9.82	18.63
39	Yttrium	89	100.0	88.905	6.53	12.23
57	Lanthanum	138 139	0.089 99.911	138.91	5.61	11.06

A certified solution of As containing 1000 mg dm^{-3} of the element in 2.5% HNO_3 was employed for the preparation of the calibration and sample solutions (Spectrascan, Teknolab A/S, Dröbak, Norway). Certified solutions of Sc and Y each containing 1000 mg dm^{-3} of the element in 2.5% HCl were used (Spectrascan, Teknolab A/S, Dröbak, Norway). A certified solution of La containing 5000 mg dm^{-3} of the element in 2.5% HNO_3 was used for the preparation of a stock solution (Spectrascan, Teknolab A/S, Dröbak, Norway). A stock solution of La containing 1000 mg dm^{-3} of the element in 2.5% HNO_3 was prepared. High purity hydrochloric acid (> 32%) and nitric acid (> 65%) (Fluka) were used for the preparation of acidic solutions. High purity water with resistivity 18.2 MΩ cm (Millipore Corporation, United States of America) was used for dilutions.

All solutions were prepared in pre-conditioned plastic laboratory ware. A-grade pipettes and volume adjustable pipettes were used for the transfer of solutions. All solutions were transferred to clean PTFE holders which were placed on the sample rack of the autosampler of the instrument.

4.4.2 Optimisation of the instrument

The instrument was optimised as described in chapter 2. A warm-up time of three hours was allowed before any analyses were performed in order for instrumental conditions to equilibrate.

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Table 4.2: Preparation of stock solutions of As, Sc, Y and La.

Element	**[Element] in certified solution (mg dm^{-3})**	**[HNO$_3$] in certified solution (% v/v)**	**[HCl] in certified solution (% v/v)**	**[Element] in stock solution (μg dm^{-3})**	**[HNO$_3$] in stock solution (% v/v)**	**[HCl] in stock solution (% v/v)**	**Volume of flask (10^{-3} dm^3)**	**Volume of certified solution to transfer (10^{-3} dm^3)**	**Volume of concentrated HNO$_3$ to add (10^{-3} dm^3)**	**Volume concentrated HCl to add (10^{-3} dm^3)**
As	1000	2.50	0.00	1000	1.00	0.00	1000	1.00	9.98	0.00
La	1000	2.50	0.00							
Y	1000	0.00	2.50							
Sc	1000	0.00	2.50							
Internal standards (i.s.)				10000	1.00	1.00	500	5.00	4.88	4.75

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Table 4.3: Preparation of A.: Arsenic calibration standards with internal standards in 1.00% v/v HNO_3,
B.1: 20 μg dm^{-3} arsenic sample solutions to study the effects of HNO_3,
B.2: 20 μg dm^{-3} arsenic sample solutions to study the effects of HCl and
B.3: 20 μg dm^{-3} arsenic sample solutions to study the effects of HNO_3 and HCl on the quantitative analysis of arsenic.

	[As] (μg dm^{-3})	Volume of flask (10^{-3} dm^3)	[HNO_3] (% v/v)	[HCl] (% v/v)	Volume of As to transfer (10^{-3} dm^3)	[internal standard] (μg dm^{-3})	Volume of internal standard solution to transfer (10^{-3} dm^3)	Volume of concentrated HNO_3 to add (10^{-3} dm^3)	Volume of concentrated HCl to add (10^{-3} dm^3)
A.	0	100	1.00	0.00	0.00	100	1.00	0.99	0.00
	5	100	1.00	0.00	0.50	100	1.00	0.99	0.00
	10	100	1.00	0.00	1.00	100	1.00	0.98	0.00
	20	100	1.00	0.00	2.00	100	1.00	0.97	0.00
	50	100	1.00	0.00	5.00	100	1.00	0.94	0.00
	100	100	1.00	0.00	10.00	100	1.00	0.89	0.00
B.1	20	100	0.10	0.00	2.00	100	1.00	0.07	0.00
	20	100	0.50	0.00	2.00	100	1.00	0.47	0.00
	20	100	1.00	0.00	2.00	100	1.00	0.97	0.00
	20	100	1.50	0.00	2.00	100	1.00	1.47	0.00
	20	100	2.00	0.00	2.00	100	1.00	1.97	0.00
	20	100	2.50	0.00	2.00	100	1.00	2.47	0.00
B.2	20	100	0.00	0.10	2.00	100	1.00	0.00	0.08
	20	100	0.00	0.50	2.00	100	1.00	0.00	0.48
	20	100	0.00	1.00	2.00	100	1.00	0.00	0.98
	20	100	0.00	1.50	2.00	100	1.00	0.00	1.48
	20	100	0.00	2.00	2.00	100	1.00	0.00	1.98
	20	100	0.00	2.50	2.00	100	1.00	0.00	2.48
B.3	20	100	0.10	0.10	2.00	100	1.00	0.07	0.08
	20	100	0.50	0.50	2.00	100	1.00	0.47	0.48
	20	100	1.00	1.00	2.00	100	1.00	0.97	0.98

Table 4.4: Operating conditions of the inductively coupled plasma mass spectrometer and settings for data acquisition.

Instrument	Spectromass-ICP
Torch	Fassel
Spray chamber	Scott-type double-pass
Nebuliser	Meinhard
Sampler cone	Ni with diameter approximately 1 mm
Skimmer cone	Ni with diameter approximately 1 mm
RF power	1350 W
Coolant argon gas flow rate	16 dm^3 min^{-1}
Auxiliary argon gas flow rate	1.5 dm^3 min^{-1}
Aerosol carrier argon gas flow rate	0.96 dm^3 min^{-1}
Sample introduction	$1.0x10^{-3}$ dm^3 min^{-1}
Dwell time	1 s
Resolution	Normal
Readings per measurement	6
Rinse time with water between samples to avoid contamination	180 s
Total pre-flush time with sample before measurement	120 s (of which the first 20 s was set at an uptake rate of approximately $3x10^{-3}$ dm^3 min^{-1})
Isotopes / masses monitored	^{35}Cl, ^{37}Cl, ^{36}Ar, ^{45}Sc, ^{89}Y, ^{139}La, mass 75, mass 77

4.4.3 *Mass scans of arsenic and the internal standards in the various acidic matrices*

Various mass scans of 20 μg dm^{-3} As in different acidic media were measured. They were performed in order to verify the validity of 1) the isotopic ratios used and 2) the mass calibration of the instrument.

4.4.4 *Data acquisition*

The intensities of the various isotopes of the internal standards and arsenic were measured. The data was then used to construct calibration curves and perform quantitative analysis of the arsenic. The operating conditions of the inductively coupled plasma mass spectrometer and settings for data acquisition are listed in table 4.4.

4.5 Results and discussion

4.5.1 Mass scans of a 20 μg dm^{-3} As solution in various acidic media

From figure 4.1 it can be seen that there is an increase in the intensities recorded for the isotopes of chlorine when the matrix contains a small amount of chloride. From figures 4.1 to 4.4 it can be seen that the intensities of ^{36}Ar, ^{45}Sc, ^{89}Y and ^{139}La are not affected by a change in the matrix. Figure 4.5 clearly shows the effect that a chloride containing matrix has on the intensity of the ^{75}As isotope as ^{40}Ar^{35}Cl forms.

From figures 4.1 to 4.5 it can also be seen that the theoretical relative abundance values correspond to the experimental values obtained thus confirming the validity of the mass calibration of the instrument.

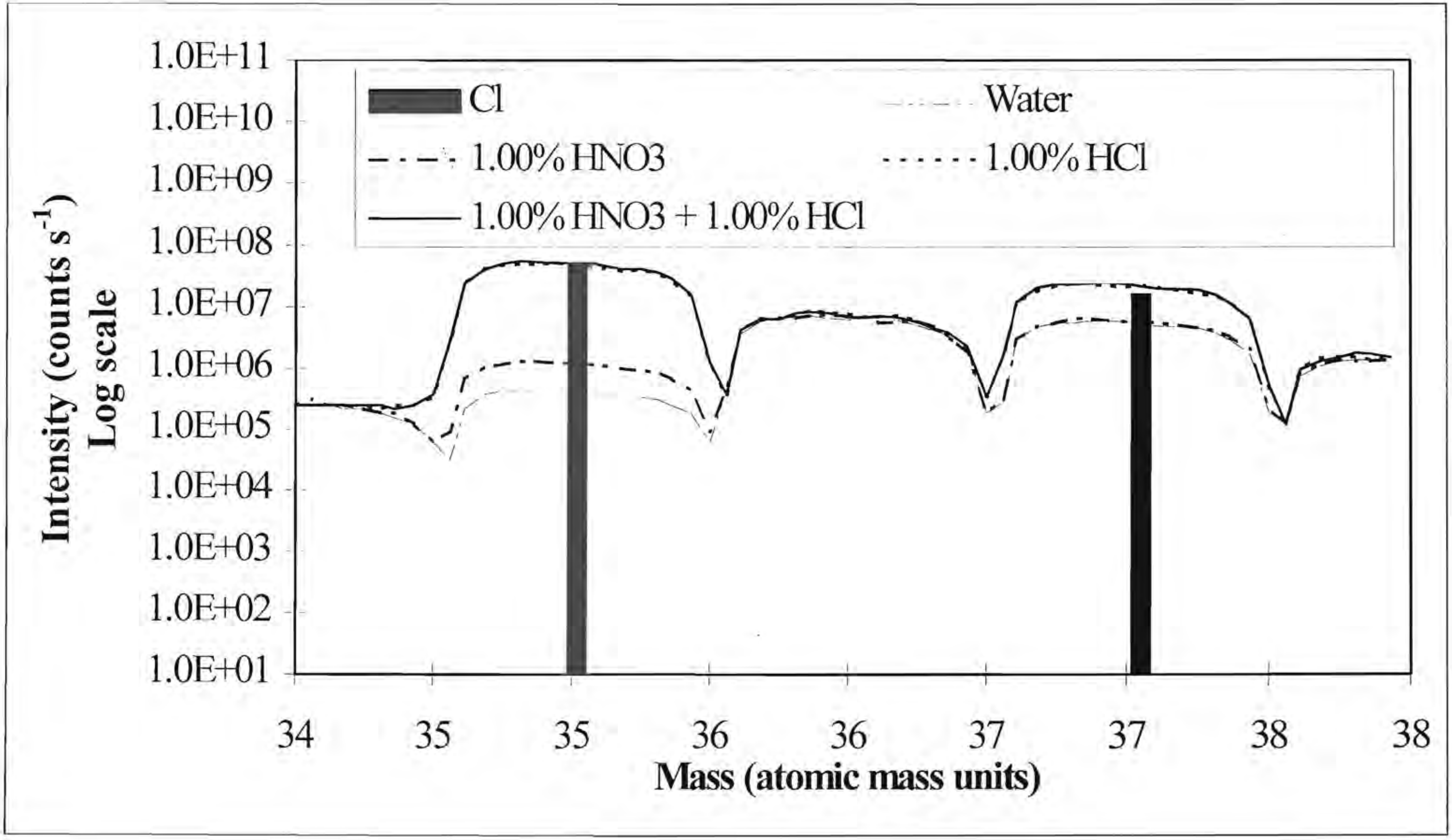

Figure 4.1: Mass scan of a solution containing 20 μg dm^{-3} As in various acidic matrices. The theoretical relative abundances of the ^{35}Cl and ^{37}Cl isotopes are shown.

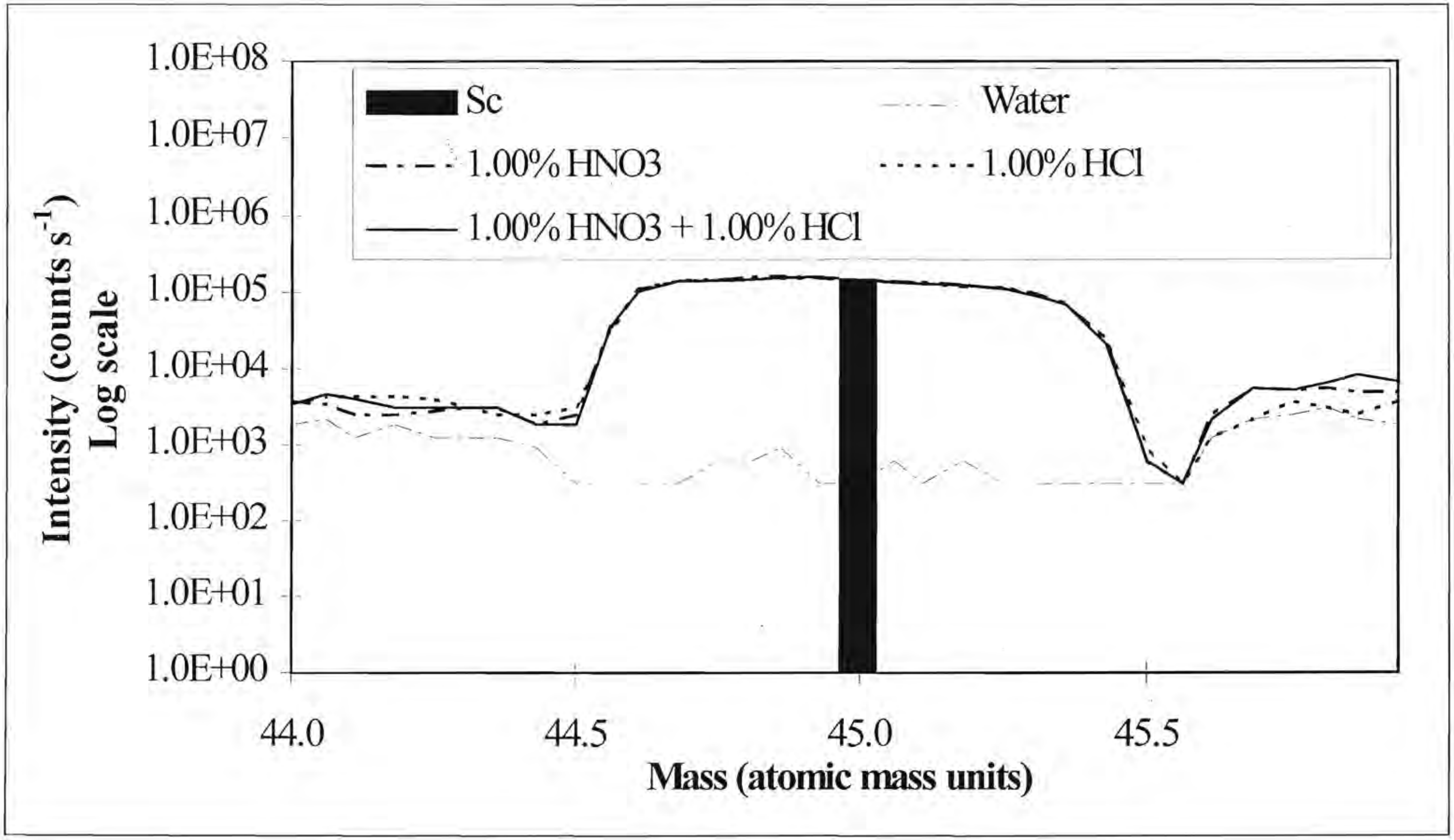

Figure 4.2: Mass scan of a solution containing 20 μg dm^{-3} As in various acidic matrices. The theoretical relative abundance of the ^{45}Sc isotope is shown.

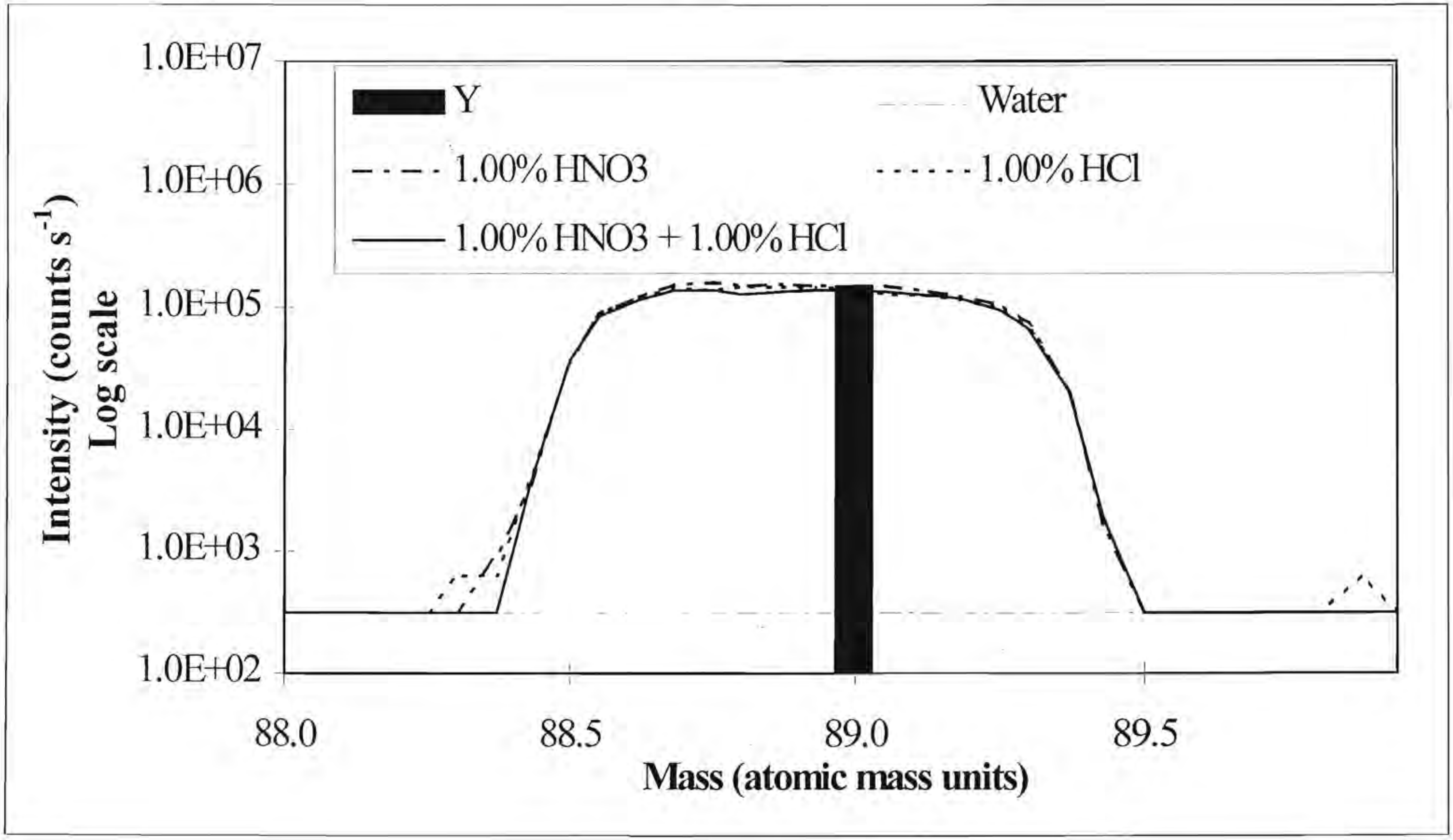

Figure 4.3: Mass scan of a solution containing 20 μg dm^{-3} As in various acidic matrices. The theoretical relative abundance of the ^{89}Y isotope is shown.

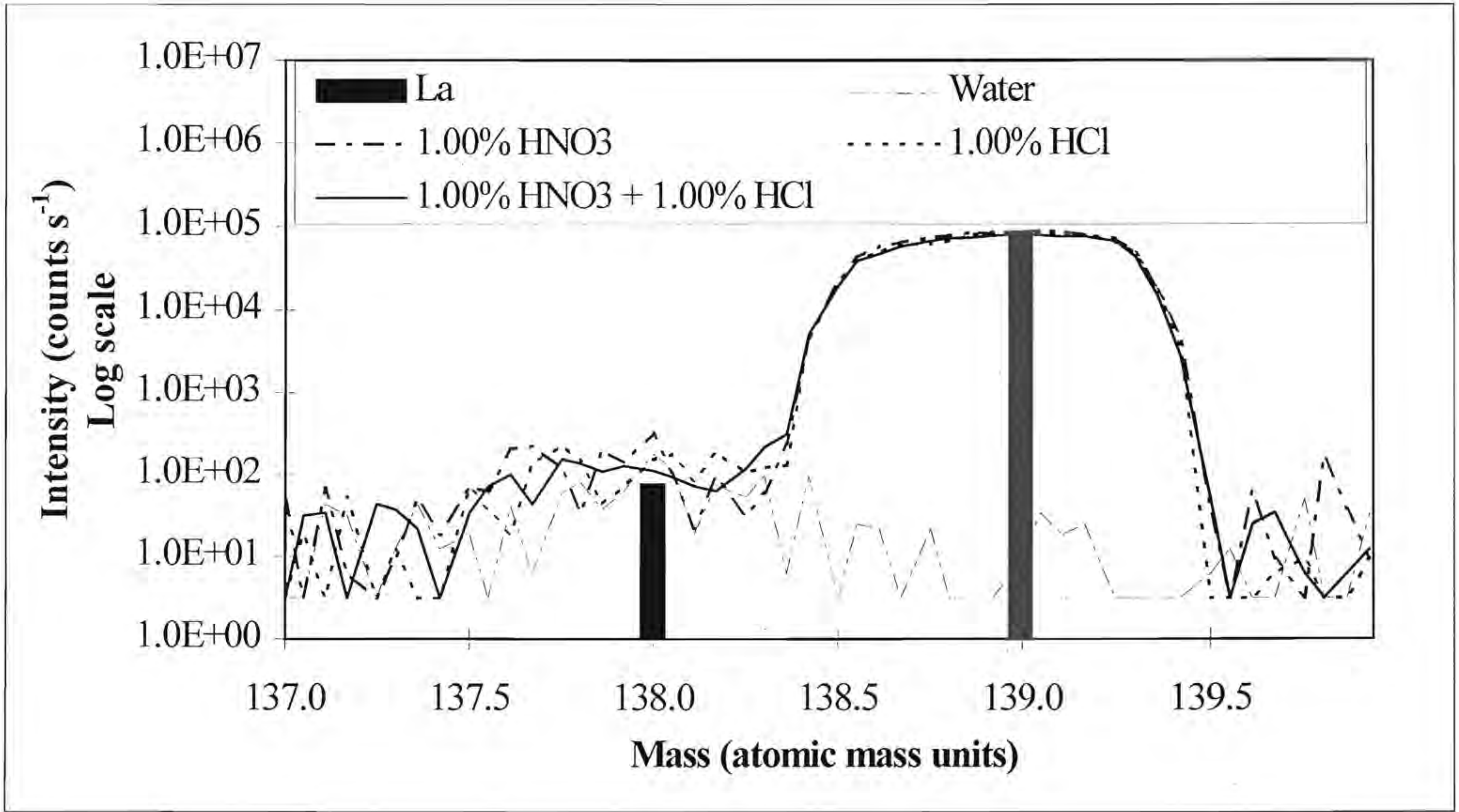

Figure 4.4: Mass scan of a solution containing 20 μg dm^{-3} As in various acidic matrices. The theoretical relative abundances of the ^{138}La and ^{139}La isotopes are shown.

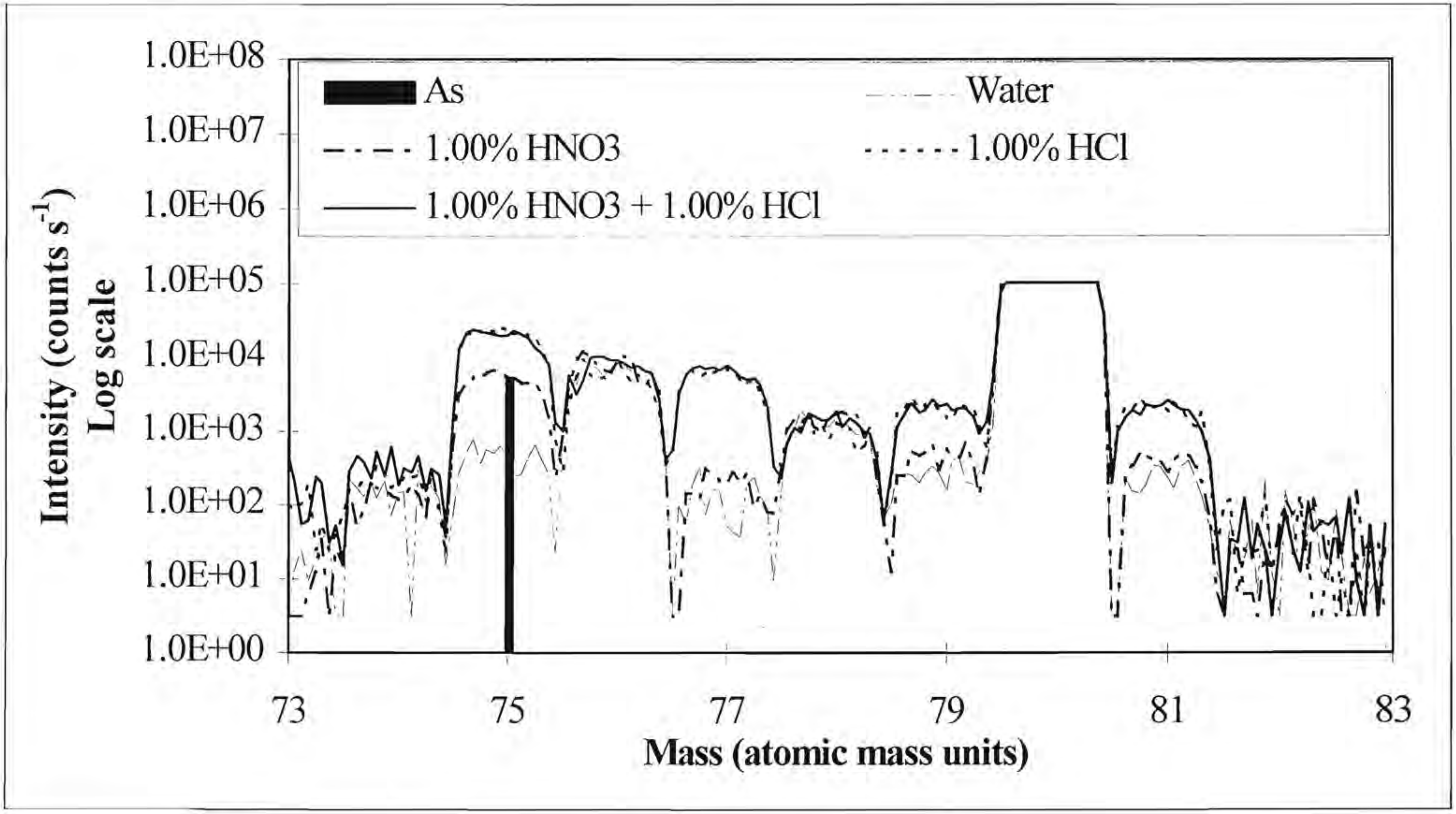

Figure 4.5: Mass scan of a solution containing 20 μg dm^{-3} As in various acidic matrices. The theoretical relative abundance of the ^{75}As isotope is shown.

4.5.2 *Analysis without employing correction factors*

As it is known that in inductively coupled plasma spectrometry a drift in the values with time occurs, it was decided to monitor such instrumental drift and to correct the values obtained from analysis for such drift. The following procedure was followed: A solution of 20 μg dm^{-3} As in 1.00% v/v HNO_3 was used to monitor the drift of the instrument with time. This solution was analysed at regular intervals during the course of the experimental run. The time difference from the analysis of the first sample was recorded in each case. First and second order mathematical curves were then fitted to the data and the obtained equations were then used to correct all the values for any time drift phenomena.

No internal standard

Calibration with the six calibration standards yielded a calibration curve with a correlation coefficient of 0.9999 and a detection limit of 0.996 μg dm^{-3} As. The results of the analysis of the prepared samples, the first and second order mathematical functions, which fitted the data of the drift control sample, and the results after drift correction was applied, can be seen in table 4.5.

It can be seen from the results that in the absence of hydrochloric acid the concentration of the nitric acid in the matrix had no effect on the analysis of the arsenic in solution. Values of approximately 20 μg dm^{-3} were obtained in matrices containing nitric acid from 0.10% v/v to 2.50% v/v. As expected the hydrochloric acid containing matrices yielded unacceptable high values.

Table 4.5: Results of quantitative determination of As using the intensities of the calibration standards for calibration. No internal standard was used. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0351x + 19.435$) and second order equation used: ($y = -0.0002x^2 + 0.0875x + 16.681$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	20.12	19.17	19.86
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.73	18.57	18.99

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.70	19.24	19.44
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.95	19.25	19.23
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.95	19.02	18.82
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.10	18.05	17.70
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.99	18.63	18.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	40.02	32.76	30.90
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	126.81	102.70	96.80
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	235.23	188.54	177.65
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	327.20	259.57	244.66
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	429.43	337.21	318.15
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	515.49	400.71	378.67
188.58	Drift control - 20 μg dm^{-3} As	28.69	22.02	20.87
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	45.43	33.46	32.23
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	151.83	110.76	107.28
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	268.09	193.73	188.76
244.08	Drift control - 20 μg dm^{-3} As	26.79	19.13	18.80
296.78	Drift control - 20 μg dm^{-3} As	29.31	19.64	20.53

^{45}Sc, ^{89}Y and ^{139}La as internal standards

The calibration curve obtained when using ^{45}Sc as internal standard yielded a correlation coefficient of 0.9999 and a detection limit of 1.066 μg dm^{-3} As. In the case of ^{89}Y as internal standard a correlation coefficient of 0.9999 was obtained with a detection limit of 0.887 μg dm^{-3} As. For ^{139}La the correlation coefficient was also 0.9999 and the detection limit was calculated to be 1.010 μg dm^{-3} As. The results of the analysis as well as the time drift corrected values can be seen in tables 4.6 to 4.8.

In all three cases the matrices containing only nitric acid resulted in acceptable values of approximately 20 μg dm^{-3}, while the hydrochloric acid containing matrices resulted in unacceptably high values.

Table 4.6: Results of quantitative determination of As using ^{45}Sc as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0138x + 19.097$) and second order equation used: ($y = -0.0001x^2 + 0.0489x + 17.255$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.11	19.39	19.89
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.45	18.62	18.92
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.62	19.70	19.84
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.34	19.33	19.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.48	19.37	19.21
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.10	18.90	18.62
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.92	19.62	19.22
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	33.44	31.75	30.33
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	107.49	101.57	96.92
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	198.93	187.09	178.43
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	272.73	255.27	243.46
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	347.81	324.01	309.18
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	414.84	384.62	367.39
188.58	Drift control - 20 μg dm^{-3} As	23.59	21.75	20.81

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	36.71	33.17	32.15
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	123.26	110.87	107.92
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	221.72	198.53	194.17
244.08	Drift control - 20 μg dm^{-3} As	21.47	19.12	18.82
296.78	Drift control - 20 μg dm^{-3} As	22.91	19.76	20.51

Table 4.7: Results of quantitative determination of As using ^{89}Y as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0223x + 18.810$) and second order equation used: ($y = -0.0001x^2 + 0.0679x + 16.414$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.07	19.26	19.90
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.64	18.67	19.06
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.03	19.91	20.09
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.37	19.09	19.07
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.75	19.31	19.11
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.15	18.57	18.23
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.92	19.18	18.69
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	35.79	32.55	30.76
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	120.47	108.78	102.68
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	233.19	209.00	197.18
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	322.11	286.59	270.42
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	423.95	374.45	353.60

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	510.18	447.36	423.04
188.58	Drift control - 20 μg dm^{-3} As	25.07	21.79	20.66
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	41.16	34.71	33.43
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	140.89	117.99	114.23
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	260.14	216.37	210.69
244.08	Drift control - 20 μg dm^{-3} As	23.57	19.44	19.08
296.78	Drift control - 20 μg dm^{-3} As	24.82	19.52	20.41

Table 4.8: Results of quantitative determination of As using ^{139}La as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0292x + 18.726$) and second order equation used: ($y = -0.0002x^2 + 0.0824x + 15.932$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.17	19.14	19.88
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.31	19.08	19.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.22	19.77	19.98
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.50	18.87	18.85
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.81	18.98	18.76
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.32	18.33	17.94
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.16	18.92	18.37
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	37.64	32.89	30.87
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	130.66	113.13	106.06
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	261.15	224.01	209.91

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	360.85	306.70	287.48
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	481.37	405.44	380.38
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	599.61	500.48	470.32
188.58	Drift control - 20 μg dm^{-3} As	26.70	22.04	20.77
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	43.98	34.97	33.55
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	156.97	123.76	119.40
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	297.13	232.30	225.54
244.08	Drift control - 20 μg dm^{-3} As	24.94	19.30	18.90
296.78	Drift control - 20 μg dm^{-3} As	26.73	19.51	20.47

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

Correlation coefficients of 0.9999 were obtained when using the ^{36}Ar and ^{37}Cl isotopes as internal standards. In the case of ^{35}Cl the correlation coefficient was 1.0000. The detection limits were calculated to be 1.062 μg dm^{-3} As, 0.493 μg dm^{-3} As and 1.057 μg dm^{-3} As in the cases of ^{36}Ar, ^{35}Cl and ^{37}Cl. The results of the analysis can be seen in tables 4.9 to 4.11.

For ^{36}Ar slightly lower values than 20 μg dm^{-3} were obtained in the case of matrices only containing various amounts of nitric acid, but after drift correction was applied acceptable values were obtained. In the case of ^{35}Cl, values of approximately 20 μg dm^{-3} were obtained for matrices containing only nitric acid, but after drift correction, values higher than 20 μg dm^{-3} were mostly obtained. ^{37}Cl as internal standard yielded values of approximately 20 μg dm^{-3} for acidic matrices not containing hydrochloric acid.

In all the cases with all three the internal standards, unacceptable values were obtained when hydrochloric acid was present in the matrix.

Table 4.9: Results of quantitative determination of As using ^{36}Ar as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0038x + 19.008$) and second order equation used: ($y = -6\text{x}10^{-5}x^2 + 0.016x + 17.969$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	18.47	19.61	19.90
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.18	18.26	18.43
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	18.02	19.19	19.27
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	18.04	19.24	19.23
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	17.85	19.06	18.96
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	17.15	18.34	18.18
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	18.28	19.57	19.32
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	29.70	32.17	31.21
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	92.60	100.44	97.37
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	159.76	173.55	168.15
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	212.49	231.19	223.95
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	268.59	292.67	283.53
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	300.65	328.11	318.00
188.58	Drift control - 20 μg dm^{-3} As	19.65	21.49	20.85
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	30.91	34.02	33.26
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	100.96	111.29	109.12
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	173.39	191.42	188.28
244.08	Drift control - 20 μg dm^{-3} As	17.09	18.91	18.68
296.78	Drift control - 20 μg dm^{-3} As	17.90	20.03	20.54

Table 4.10: Results of quantitative determination of As using ^{35}Cl as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = -0.040x + 19.880$) and second order equation used: ($y = 0.0003x^2 - 0.1458x + 25.435$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.81	21.89	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.43	21.82	20.73
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.08	22.93	22.38
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.85	23.05	23.11
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.30	23.97	24.69
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.59	23.54	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.36	24.91	27.01
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.16	3.04	3.86
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	0.14	0.20	0.26
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	-0.17	-0.25	-0.32
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	-0.42	-0.63	-0.82
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	-0.47	-0.72	-0.95
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	-0.60	-0.94	-1.24
188.58	Drift control - 20 μg dm^{-3} As	7.47	12.12	15.92
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.67	4.82	5.98
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	0.46	0.85	1.02
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	0.03	0.06	0.07
244.08	Drift control - 20 μg dm^{-3} As	11.87	23.47	26.29
296.78	Drift control - 20 μg dm^{-3} As	9.37	23.39	17.80

Table 4.11: Results of quantitative determination of As using ^{37}Cl as internal standard. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0072x + 18.948$) and second order equation used: ($y = -3\times10^{-5}x^2 + 0.0185x + 18.353$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.06	19.78	19.94
51.83	20 μg dm^{-3} As in 0.10% v/v HNO$_3$	18.69	19.35	19.44
59.10	20 μg dm^{-3} As in 0.50% v/v HNO$_3$	19.11	19.73	19.76
66.42	20 μg dm^{-3} As in 1.00% v/v HNO$_3$	18.96	19.52	19.49
73.68	20 μg dm^{-3} As in 1.50% v/v HNO$_3$	18.72	19.22	19.14
80.95	20 μg dm^{-3} As in 2.00% v/v HNO$_3$	17.82	18.25	18.14
88.22	20 μg dm^{-3} As in 2.50% v/v HNO$_3$	18.56	18.96	18.80
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	27.36	27.40	26.85
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	45.34	45.28	44.34
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	51.20	50.99	49.90
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	51.20	50.87	49.75
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	52.92	52.43	51.26
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	51.55	50.94	49.79
188.58	Drift control - 20 μg dm^{-3} As	21.06	20.74	20.27
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	29.71	28.94	28.34
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	51.28	49.82	48.82
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	56.79	55.03	53.98
244.08	Drift control - 20 μg dm^{-3} As	20.17	19.48	19.14
296.78	Drift control - 20 μg dm^{-3} As	21.08	19.99	19.88

4.5.3 Effect of using molecular (mass 75 / mass 77) corrections in a 0.10% v/v HCl matrix on the quantitative determination of arsenic

This factor depends upon the formation of the $^{40}Ar^{35}Cl$ and $^{40}Ar^{37}Cl$ molecular interferences at masses 75 and 77. It is calculated by measuring the intensities at masses 75 and 77 for a blank solution containing no arsenic or chlorine and for a solution containing a small amount of chlorine but no arsenic. The ratio of the intensities at the two masses is then determined after the blank values have been subtracted. It is then assumed that the formation of the dimers is constant in the plasma and the intensity at mass 75 can subsequently be corrected for the contribution by the $^{40}Ar^{35}Cl$ dimer at mass 75.

The correction factor when a blank and a 0.10% v/v HCl solution were measured was 3.275. (The theoretical ratio of the relative abundances of the ^{35}Cl to the ^{37}Cl isotopes is 3.087.)

No internal standard

When only the correction factor of 3.275 was used with no internal standard the correlation coefficient of the calibration curve was 1.0000 and the detection limit was 1.706 μg dm^{-3} As. The results of the analysis can be seen in table 4.12.

The matrices containing only nitric acid and no hydrochloric acid yielded values of approximately 20 μg dm^{-3}. Due to the applied correction the values obtained for the solutions containing 0.10% v/v to 1.00% v/v HCl, (0.10% v/v HNO_3 + 0.10% v/v HCl) and (1.00% v/v HNO_3 + 1.00% v/v HCl) were acceptable.

Table 4.12: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0081x + 20.274$) and second order equation used: ($y = -1\text{x}10^{-5}x^2 + 0.0125x + 20.039$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.59	19.96	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.31	19.35

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.12	20.36	20.37
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.44	20.60	20.59
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.15	20.11
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.44	19.53	19.48
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.22	20.15
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.21	18.86	18.70
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.26	17.00	16.84
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	18.30	16.99	16.82
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	10.61	9.82	9.72
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	15.55	14.36	14.21
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	9.35	8.61	8.52
188.58	Drift control - 20 μg dm^{-3} As	21.77	19.97	19.75
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.98	18.12	17.92
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.80	15.19	15.02
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	19.44	17.53	17.34
244.08	Drift control - 20 μg dm^{-3} As	22.51	20.23	20.01
296.78	Drift control - 20 μg dm^{-3} As	22.47	19.82	19.65

^{45}Sc, ^{89}Y and ^{139}La as internal standards

Calibration curves constructed when employing ^{45}Sc, ^{89}Y and ^{139}La as internal standards each resulted in a correlation coefficients of 1.0000 with detection limits of 1.759 μg dm^{-3} As, 1.718 μg dm^{-3} As and 1.711 μg dm^{-3} As respectively. The results of the analysis can be seen in tables 4.13 to 4.15.

In all three cases the nitric acid matrices yielded values of approximately 20 μg dm^{-3} As.

Table 4.13: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0059x + 19.915$) and second order equation used: ($y = 2x10^{-5}x^2 - 0.0128x + 20.277$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	20.12	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.94	19.32	19.26
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.24	20.69	20.66
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.10	20.59	20.60
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.35	20.39
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.64	20.20	20.27
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.36	20.99	21.09
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.23	18.07	18.28
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	15.61	16.41	16.60
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	15.58	16.41	16.61
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	8.94	9.44	9.55
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	12.72	13.45	13.62
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	7.64	8.10	8.20
188.58	Drift control - 20 μg dm^{-3} As	18.42	19.59	19.83
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	16.52	17.75	17.93
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	13.80	14.86	15.00
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	16.19	17.48	17.63
244.08	Drift control - 20 μg dm^{-3} As	18.67	20.21	20.36
296.78	Drift control - 20 μg dm^{-3} As	18.21	20.05	19.96

Table 4.14: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 4\text{x}10^{-5}x + 19.686$) and second order equation used: ($y = -3\text{x}10^{-6}x^2 + 0.0009x + 19.638$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.71	20.03	20.04
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.09	19.39	19.40
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.58	20.90	20.91
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.10	20.42	20.42
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.03	20.35	20.35
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.65	19.96	19.96
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.33	20.65	20.65
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.31	18.60	18.58
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	17.41	17.68	17.67
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	18.14	18.43	18.41
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	10.45	10.62	10.61
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	15.36	15.60	15.59
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	9.26	9.40	9.40
188.58	Drift control - 20 μg dm^{-3} As	19.39	19.70	19.69
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.30	18.59	18.59
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	15.67	15.91	15.92
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	18.88	19.18	19.19
244.08	Drift control - 20 μg dm^{-3} As	20.19	20.50	20.52
296.78	Drift control - 20 μg dm^{-3} As	19.48	19.78	19.84

Table 4.15: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0048x + 19.636$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.011x + 19.308$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.79	19.94	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.65	19.76	19.82
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.73	20.81	20.85
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	20.25	20.26
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.09	20.10	20.08
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.80	19.78	19.73
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.53	20.47	20.40
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.19	18.88	18.75
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.85	18.52	18.38
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	20.27	19.88	19.74
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	11.68	11.44	11.36
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	17.40	17.01	16.88
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	10.81	10.55	10.47
188.58	Drift control - 20 μg dm^{-3} As	20.49	19.95	19.82
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.46	18.81	18.75
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	17.40	16.79	16.75
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	21.50	20.71	20.69
244.08	Drift control - 20 μg dm^{-3} As	21.19	20.37	20.38
296.78	Drift control - 20 μg dm^{-3} As	20.77	19.73	19.96

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

Correlation coefficients of 0.9998, 1.0000 and 0.9999 and detection limits of 1.939 μg dm^{-3} As, 1.207 μg dm^{-3} As and 1.824 μg dm^{-3} As respectively were obtained when using ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards for the calibration curves. Tables 4.16 to 4.18 show the results of the analysis.

The matrices containing only nitric acid yielded values of approximately 20 μg dm^{-3} As. The correction procedure resulted in values below 20 μg dm^{-3} for matrices containing hydrochloric acid.

Table 4.16: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0183x + 19.898$) and second order equation used: ($y = 6\text{x}10^{-5}x^2 - 0.0369x + 20.874$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.36	20.29	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.01	19.01	18.84
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.02	20.22	20.13
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.14	20.49	20.48
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.59	20.04	20.12
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.13	19.68	19.83
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.10	20.89	21.12
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.25	17.64	18.12
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	12.96	15.11	15.53
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	11.99	14.09	14.48
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	6.41	7.59	7.80
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	9.27	11.06	11.37

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	5.01	6.03	6.19
188.58	Drift control - 20 μg dm^{-3} As	15.76	19.16	19.64
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.87	17.47	17.71
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	10.82	13.75	13.88
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	12.15	15.58	15.67
244.08	Drift control - 20 μg dm^{-3} As	15.50	20.09	20.08
296.78	Drift control - 20 μg dm^{-3} As	14.81	20.47	19.47

Table 4.17: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0432x + 20.304$) and second order equation used: ($y = 0.0003x^2 - 0.1481x + 25.714$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	20.04	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.53	20.53
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.32	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.21	23.18	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.60	24.37
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.73	23.48	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.75	26.93
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.99	4.23	5.45
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.26	1.83	2.39
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.08	1.60	2.13

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.98	1.48	1.99
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.98	1.53	2.08
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.95	1.51	2.07
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.34	16.99
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.95	5.45	7.28
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.22	2.32	3.04
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.09	2.14	2.73
244.08	Drift control - 20 μg dm^{-3} As	11.39	23.34	28.74
296.78	Drift control - 20 μg dm^{-3} As	8.87	23.69	20.20

Table 4.18: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.10% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0108x + 19.876$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0344x + 21.114$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.78	20.40	20.06
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.20	19.88	19.68
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.87	20.66	20.56
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.83	20.70	20.72
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.24	20.17	20.29
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.61	19.59	19.81
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.26	20.35	20.68
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.32	15.62	16.25

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	6.93	7.60	7.91
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	4.39	4.83	5.03
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	1.99	2.20	2.30
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	2.30	2.55	2.66
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	1.28	1.43	1.49
188.58	Drift control - 20 μg dm^{-3} As	16.69	18.71	19.50
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.55	15.48	16.00
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	6.02	6.91	7.12
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	4.51	5.20	5.34
244.08	Drift control - 20 μg dm^{-3} As	17.71	20.54	20.97
296.78	Drift control - 20 μg dm^{-3} As	16.93	20.31	19.83

4.5.4 Effect of using molecular (mass 75 / mass 77) corrections in a 0.50% v/v HCl matrix on the quantitative determination of arsenic

No internal standard

Correction factor of 3.202 was calculated after measuring a blank and a 0.50% v/v HCl solution. When not using an internal standard a correlation coefficient of 1.0000 was calculated with a detection limit of 1.687 μg dm^{-3} As. The results are in table 4.19.

The time drift corrected values obtained for the samples containing only nitric acid as matrix yielded acceptable values of approximately 20 μg dm^{-3} As. Acceptable values were obtained for samples containing 0.10% v/v HCl and 0.50% v/v HCl.

Table 4.19: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0087x + 20.256$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0142x + 19.965$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.58	19.94	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.30	19.35
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.11	20.33	20.36
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.43	20.57	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.12	20.11
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.50	19.48
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.18	20.15
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.64	19.21	19.13
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.64	19.15	19.08
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.07	21.34	21.26
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	17.57	16.20	16.15
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	24.65	22.67	22.60
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	20.47	18.77	18.73
188.58	Drift control - 20 μg dm^{-3} As	21.92	20.02	19.99
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.54	18.53	18.57
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	19.77	17.78	17.84
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	24.90	22.34	22.44
244.08	Drift control - 20 μg dm^{-3} As	22.60	20.20	20.33
296.78	Drift control - 20 μg dm^{-3} As	22.62	19.81	20.18

^{45}Sc, ^{89}Y and ^{139}La as internal standards

Regression correlation coefficients of 1.0000 were obtained for the calibration curves and detection limits of 1.730 μg dm^{-3} As, 1.697 μg dm^{-3} As and 1.689 μg dm^{-3} As were calculated respectively for ^{45}Sc, ^{89}Y and ^{139}La as internal standards. The results of the analyses can be seen in tables 4.20 to 4.22.

In all three cases acceptable values of approximately 20 μg dm^{-3} As were obtained when the matrices contained only nitric acid. In all three cases some of the matrices containing hydrochloric acid yielded values of approximately 20 μg dm^{-3} As, but the correction procedure was not successful for all these matrices.

Table 4.20: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0055x + 19.897$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0115x + 20.210$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.75	20.10	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.93	19.31	19.25
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.23	20.67	20.64
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.56	20.56
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.33	20.36
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.62	20.18	20.22
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.96	21.03
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.59	18.40	18.54
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	17.63	18.49	18.62
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	19.60	20.60	20.75
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	14.73	15.51	15.62

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	20.07	21.18	21.33
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	16.58	17.53	17.65
188.58	Drift control - 20 μg dm^{-3} As	18.53	19.65	19.77
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	16.96	18.15	18.19
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	16.20	17.38	17.39
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	20.71	22.26	22.25
244.08	Drift control - 20 μg dm^{-3} As	18.73	20.19	20.15
296.78	Drift control - 20 μg dm^{-3} As	18.31	20.05	19.73

Table 4.21: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0005x + 19.667$) and second order equation used: ($y = -6\text{x}10^{-6}x^2 + 0.0024x + 19.568$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.70	20.01	20.04
51.83	20 μg dm^{-3} As in 0.10% v/v HNO$_3$	19.08	19.38	19.39
59.10	20 μg dm^{-3} As in 0.50% v/v HNO$_3$	20.56	20.88	20.89
66.42	20 μg dm^{-3} As in 1.00% v/v HNO$_3$	20.08	20.39	20.39
73.68	20 μg dm^{-3} As in 1.50% v/v HNO$_3$	20.03	20.33	20.32
80.95	20 μg dm^{-3} As in 2.00% v/v HNO$_3$	19.64	19.93	19.92
88.22	20 μg dm^{-3} As in 2.50% v/v HNO$_3$	20.32	20.62	20.60
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.69	18.94	18.90
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.67	19.93	19.88

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	22.87	23.16	23.10
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	17.30	17.52	17.47
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	24.34	24.64	24.58
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	20.26	20.51	20.46
188.58	Drift control - 20 μg dm^{-3} As	19.52	19.75	19.71
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.80	19.02	18.99
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.42	18.62	18.60
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	24.18	24.45	24.43
244.08	Drift control - 20 μg dm^{-3} As	20.26	20.48	20.47
296.78	Drift control - 20 μg dm^{-3} As	19.60	19.78	19.84

Table 4.22: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0053x + 19.616$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0126x + 19.234$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	19.92	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.64	19.75	19.81
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.72	20.79	20.81
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.19	20.22	20.21
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.07	20.03
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.79	19.74	19.67
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.52	20.43	20.33

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.59	19.23	19.00
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.30	20.88	20.61
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	25.56	25.00	24.68
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	19.36	18.89	18.64
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	27.59	26.88	26.52
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	23.75	23.09	22.78
188.58	Drift control - 20 μg dm^{-3} As	20.62	20.01	19.74
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.00	19.25	19.01
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	20.47	19.66	19.43
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	27.56	26.42	26.13
244.08	Drift control - 20 μg dm^{-3} As	21.28	20.35	20.15
296.78	Drift control - 20 μg dm^{-3} As	20.90	19.73	19.71

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

In the cases of ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards regression correlation coefficients of 0.9998, 1.0000 and 0.9999 were obtained. It resulted in detection limits of 1.915 μg dm^{-3} As, 1.182 μg dm^{-3} As and 1.803 μg dm^{-3} As respectively. Tables 4.23 to 4.25 show the results of the analyses.

Nitric acid matrices yielded values of 20 μg dm^{-3} in the cases of ^{36}Ar and ^{37}Cl. Time drift corrected values for ^{35}Cl resulted in too high values for the 20 μg dm^{-3} As samples. For ^{36}Ar the results show slightly too low values for hydrochloric acid containing matrices. In the cases of ^{35}Cl and ^{37}Cl as internal standards very poor results were obtained for hydrochloric acid containing matrices.

Table 4.23: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.018x + 19.878$) and second order equation used: ($y = 5\text{x}10^{-5}x^2 - 0.0357x + 20.810$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.34	20.28	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.00	19.00	18.85
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.00	20.20	20.13
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.11	20.46	20.49
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.57	20.02	20.13
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.10	19.66	19.84
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.08	20.86	21.14
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.57	17.98	18.60
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	14.70	17.11	17.73
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	15.22	17.86	18.52
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	10.92	12.91	13.40
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	14.94	17.80	18.50
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	11.48	13.78	14.33
188.58	Drift control - 20 μg dm^{-3} As	15.84	19.22	19.98
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.24	17.89	18.52
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	12.79	16.21	16.75
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	15.68	20.04	20.65
244.08	Drift control - 20 μg dm^{-3} As	15.54	20.07	20.61
296.78	Drift control - 20 μg dm^{-3} As	14.87	20.47	20.35

Table 4.24: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.294$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.708$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.54	20.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	23.17	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.60	24.38
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.72	23.47	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.75	26.94
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.98	4.21	5.42
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.24	1.79	2.35
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.06	1.56	2.08
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.95	1.43	1.93
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.95	1.48	2.01
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.91	1.45	1.99
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.33	17.00
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.44	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.20	2.28	3.00
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.06	2.09	2.68
244.08	Drift control - 20 μg dm^{-3} As	11.40	23.33	28.79
296.78	Drift control - 20 μg dm^{-3} As	8.88	23.66	20.24

Table 4.25: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 0.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0105x + 19.856$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0332x + 21.053$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	20.39	20.05
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.19	19.87	19.66
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.85	20.64	20.53
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.81	20.68	20.68
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.23	20.15	20.25
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.59	19.56	19.75
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.24	20.33	20.61
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.61	15.91	16.47
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.78	8.51	8.81
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	5.41	5.95	6.16
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.07	3.39	3.52
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	3.41	3.77	3.91
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	2.38	2.65	2.75
188.58	Drift control - 20 μg dm^{-3} As	16.79	18.78	19.43
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.90	15.84	16.22
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.01	8.03	8.19
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	5.66	6.51	6.61
244.08	Drift control - 20 μg dm^{-3} As	17.76	20.54	20.75
296.78	Drift control - 20 μg dm^{-3} As	17.02	20.33	19.60

4.5.5 Effect of using molecular (mass 75 / mass 77) corrections in a 1.00% v/v HCl matrix on the quantitative determination of arsenic

No internal standard

A correction factor of 3.145 was obtained in the case of a matrix of 1.00% v/v HCl. A calibration correlation coefficient of 1.0000 and a detection limit of 1.671 μg dm^{-3} As resulted. The results of the analysis of the 20 μg dm^{-3} As samples are tabulated in table 4.26.

Good results were obtained for matrices only containing 20 μg dm^{-3} As and nitric acid. Acceptable results were obtained for samples in the cases of hydrochloric acid matrices of low concentration.

Table 4.26: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0091x + 20.241$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0155x + 19.906$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.57	19.93	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.97	19.29	19.34
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.10	20.31	20.34
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.42	20.55	20.55
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.10	20.08
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.48	19.43
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.21	20.16	20.09
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.99	19.49	19.34
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	22.55	20.88	20.71
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	26.88	24.81	24.61
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	23.13	21.28	21.11

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	31.92	29.28	29.05
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	29.37	26.86	26.65
188.58	Drift control - 20 μg dm^{-3} As	22.04	20.08	19.93
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.99	18.87	18.78
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	22.14	19.85	19.77
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	29.27	26.16	26.09
244.08	Drift control - 20 μg dm^{-3} As	22.68	20.19	20.16
296.78	Drift control - 20 μg dm^{-3} As	22.74	19.83	20.00

^{45}Sc, ^{89}Y and ^{139}La as internal standards

All the calibration curves yielded correlation coefficients of 1.0000 and detection limits of 1.724 μg dm^{-3} As, 1.680 μg dm^{-3} As and 1.673 μg dm^{-3} As were calculated respectively for the three internal standards. The results of the analyses are listed in tables 4.27 to 4.29.

In all three cases values of 20 μg dm^{-3} As were obtained for samples containing only nitric acid as matrix. When using any of these three elements as internal standards for arsenic analysis of solutions containing hydrochloric acid in the matrix, the correction procedure proved to be successful only when the hydrochloric acid is present at low concentrations.

Table 4.27: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0052x + 19.883$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0104x + 20.157$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.74	20.09	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.92	19.30	19.24

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.22	20.65	20.62
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.07	20.54	20.52
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.81	20.32	20.32
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.61	20.16	20.17
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.34	20.94	20.97
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.87	18.67	18.73
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.24	20.15	20.21
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	22.82	23.94	24.00
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	19.36	20.35	20.39
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	25.96	27.34	27.38
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	23.73	25.04	25.06
188.58	Drift control - 20 μg dm^{-3} As	18.62	19.71	19.70
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	17.32	18.48	18.39
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.12	19.38	19.25
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	24.32	26.06	25.84
244.08	Drift control - 20 μg dm^{-3} As	18.78	20.18	19.97
296.78	Drift control - 20 μg dm^{-3} As	18.39	20.06	19.53

Table 4.28: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0009x + 19.652$) and second order equation used: ($y = -8\times10^{-6}x^2 + 0.0036x + 19.511$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.69	20.00	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.07	19.36	19.38
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.56	20.86	20.87
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.07	20.36	20.36
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.02	20.31	20.29
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.63	19.91	19.88
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.32	20.59	20.56
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.00	19.21	19.13
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.48	21.71	21.62
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	26.64	26.92	26.81
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	22.78	23.00	22.90
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	31.51	31.82	31.68
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	29.06	29.33	29.21
188.58	Drift control - 20 μg dm^{-3} As	19.62	19.79	19.71
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.21	19.35	19.29
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	20.62	20.77	20.70
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	28.42	28.62	28.54
244.08	Drift control - 20 μg dm^{-3} As	20.32	20.45	20.41
296.78	Drift control - 20 μg dm^{-3} As	19.69	19.77	19.82

Table 4.29: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0057x + 19.600$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0138x + 19.175$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	19.91	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.64	19.74	19.80
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.71	20.77	20.79
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.18	20.20	20.17
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.06	19.99
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.78	19.72	19.62
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.51	20.41	20.27
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.91	19.51	19.21
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	23.27	22.75	22.38
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	29.80	29.07	28.58
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	25.49	24.82	24.39
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	35.74	34.74	34.11
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	34.09	33.06	32.46
188.58	Drift control - 20 μg dm^{-3} As	20.73	20.06	19.68
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.43	19.59	19.24
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	22.92	21.94	21.54
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	32.40	30.95	30.40
244.08	Drift control - 20 μg dm^{-3} As	21.34	20.33	19.99
296.78	Drift control - 20 μg dm^{-3} As	21.01	19.73	19.53

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

Calibration curves constructed using these three internal standards yielded correlation coefficients of 0.9998, 1.0000 and 0.9999 respectively. Detection limits were calculated to be 1.895 μg dm^{-3} As, 1.162 μg dm^{-3} As and 1.786 μg dm^{-3} As for the cases of ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards. Results of analyses using these internal standards are listed in tables 4.30 to 4.32.

Samples containing only nitric acid as matrix yielded good results in all three cases, but after drift correction was applied results for ^{35}Cl as internal standard yielded too high values. In the cases of samples containing hydrochloric acid in the matrix, ^{35}Cl and ^{37}Cl as internal standards yielded very poor results. However, in the case of ^{36}Ar acceptable results were obtained except in the matrices: 2.00% v/v HCl and (1.00% v/v HNO_3 + 1.00% v/v HCl).

Table 4.30: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0177x + 19.863$) and second order equation used: ($y = 5\text{x}10^{-5}x^2 - 0.0348x + 20.759$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.33	20.27	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.98	18.98	18.84
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	18.98	20.18	20.11
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.09	20.44	20.46
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.56	20.00	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.09	19.63	19.80
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.07	20.83	21.09
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.82	18.24	18.81
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	16.10	18.70	19.31
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	17.81	20.85	21.55

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	14.52	17.13	17.72
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	19.48	23.16	23.96
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	16.65	19.95	20.65
188.58	Drift control - 20 μg dm^{-3} As	15.91	19.26	19.92
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	14.54	18.21	18.73
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	14.37	18.14	18.62
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	18.50	23.56	24.11
244.08	Drift control - 20 μg dm^{-3} As	15.56	20.03	20.42
296.78	Drift control - 20 μg dm^{-3} As	14.93	20.44	20.13

Table 4.31: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.287$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.703$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.25
51.83	20 μg dm^{-3} As in 0.10% v/v HNO$_3$	19.45	21.55	20.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO$_3$	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO$_3$	20.19	23.18	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO$_3$	20.21	23.62	24.39
80.95	20 μg dm^{-3} As in 2.00% v/v HNO$_3$	19.72	23.48	24.90
88.22	20 μg dm^{-3} As in 2.50% v/v HNO$_3$	20.41	24.76	26.95
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.96	4.19	5.40

Time difference (minutes)	**Sample name**	**[As] ($\mu g\ dm^{-3}$)**	**Corrected with first order drift curve ($\mu g\ dm^{-3}$)**	**Corrected with second order drift curve ($\mu g\ dm^{-3}$)**
149.82	20 $\mu g\ dm^{-3}$ As in 0.50% v/v HCl	1.22	1.76	2.31
157.18	20 $\mu g\ dm^{-3}$ As in 1.00% v/v HCl	1.03	1.53	2.04
164.55	20 $\mu g\ dm^{-3}$ As in 1.50% v/v HCl	0.92	1.40	1.88
171.92	20 $\mu g\ dm^{-3}$ As in 2.00% v/v HCl	0.93	1.44	1.96
179.30	20 $\mu g\ dm^{-3}$ As in 2.50% v/v HCl	0.88	1.41	1.93
188.58	Drift control - 20 $\mu g\ dm^{-3}$ As	7.50	12.33	17.00
220.02	20 $\mu g\ dm^{-3}$ As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.93	5.43	7.26
227.40	20 $\mu g\ dm^{-3}$ As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.19	2.26	2.97
234.78	20 $\mu g\ dm^{-3}$ As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.04	2.05	2.63
244.08	Drift control - 20 $\mu g\ dm^{-3}$ As	11.41	23.36	28.83
296.78	Drift control - 20 $\mu g\ dm^{-3}$ As	8.89	23.71	20.27

Table 4.32: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0101x + 19.839$) and second order equation used: ($y = 7\times10^{-5}x^2 - 0.0323x + 21.005$)

Time difference (minutes)	**Sample name**	**[As] ($\mu g\ dm^{-3}$)**	**Corrected with first order drift curve ($\mu g\ dm^{-3}$)**	**Corrected with second order drift curve ($\mu g\ dm^{-3}$)**
44.57	Drift control - 20 $\mu g\ dm^{-3}$ As	19.75	20.38	20.05
51.83	20 $\mu g\ dm^{-3}$ As in 0.10% v/v HNO_3	19.18	19.86	19.65
59.10	20 $\mu g\ dm^{-3}$ As in 0.50% v/v HNO_3	19.84	20.62	20.52
66.42	20 $\mu g\ dm^{-3}$ As in 1.00% v/v HNO_3	19.80	20.66	20.65
73.68	20 $\mu g\ dm^{-3}$ As in 1.50% v/v HNO_3	19.22	20.13	20.22
80.95	20 $\mu g\ dm^{-3}$ As in 2.00% v/v HNO_3	18.58	19.53	19.71

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.23	20.30	20.57
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.84	16.13	16.65
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	8.45	9.22	9.53
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	6.23	6.83	7.06
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.94	4.33	4.48
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	4.29	4.74	4.90
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	3.26	3.62	3.74
188.58	Drift control - 20 μg dm^{-3} As	16.86	18.81	19.38
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.18	16.10	16.41
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.81	8.90	9.04
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	6.57	7.53	7.61
244.08	Drift control - 20 μg dm^{-3} As	17.80	20.50	20.59
296.78	Drift control - 20 μg dm^{-3} As	17.09	20.30	19.44

4.5.6 Effect of using molecular (mass 75 / mass 77) corrections in a 1.50% v/v HCl matrix on the quantitative determination of arsenic

No internal standard

A correction factor of 3.240 was obtained using a 1.50% v/v HCl solution. In the case of no internal standard, the calibration curve yielded a correlation coefficient of 1.0000 and a detection limit of 1.697 μg dm^{-3} As was calculated. The results of the analyses are shown in table 4.33.

Samples prepared from only arsenic and nitric acid yielded values of near to 20 μg dm^{-3}. Acceptable values were obtained for samples containing 0.10% v/v to 1.00% v/v HCl and the two samples with matrices (0.10% v/v HNO_3 + 0.10% v/v HCl) and (1.00% v/v HNO_3 + 1.00% v/v HCl).

Table 4.33: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0084x + 20.265$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0133x + 20.004$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.58	19.95	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.31	19.36
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.12	20.34	20.38
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.43	20.59	20.61
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.13	20.14
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.44	19.52	19.51
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.20	20.19
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.42	19.03	19.00
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.40	18.03	18.01
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	20.58	19.07	19.05
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	13.94	12.88	12.87
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	19.90	18.34	18.34
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	14.67	13.48	13.49
188.58	Drift control - 20 μg dm^{-3} As	21.84	19.99	20.04
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.25	18.32	18.44
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.22	16.43	16.57
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	22.05	19.83	20.02
244.08	Drift control - 20 μg dm^{-3} As	22.56	20.22	20.45
296.78	Drift control - 20 μg dm^{-3} As	22.54	19.81	20.32

^{45}Sc, ^{89}Y and ^{139}La as internal standards

In all these three cases correlation coefficients of 1.0000 were obtained for the calibration curves. Detection limits of 1.750 μg dm^{-3} As, 1.708 μg dm^{-3} As and 1.701 μg dm^{-3} As were calculated respectively. The results of the analyses when using the blank correction factor of a 1.50% v/v HCl solution together with ^{45}Sc, ^{89}Y and ^{139}La as internal standards can be seen in tables 4.34 to 4.36.

Using any of the three isotopes as internal standards values of approximately 20 μg dm^{-3} were obtained when the matrices of the samples comprised of only nitric acid. In some cases where the sample matrix contained hydrochloric acid the correction procedure proved to be successful for all three isotopes as internal standards, especially when the concentration of the hydrochloric acid was low.

Table 4.34: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0057x + 19.906$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0122x + 20.245$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	20.11	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.94	19.31	19.26
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.23	20.68	20.65
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.09	20.58	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.34	20.38
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.63	20.19	20.25
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.98	21.06
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.40	18.23	18.40
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	16.58	17.40	17.57
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	17.50	18.41	18.60

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	11.71	12.34	12.47
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	16.23	17.15	17.33
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	11.91	12.62	12.74
188.58	Drift control - 20 μg dm^{-3} As	18.47	19.62	19.81
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	16.73	17.94	18.06
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	14.95	16.06	16.16
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	18.35	19.77	19.86
244.08	Drift control - 20 μg dm^{-3} As	18.70	20.20	20.26
296.78	Drift control - 20 μg dm^{-3} As	18.26	20.05	19.86

Table 4.35: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0003x + 19.677$) and second order equation used: ($y = -4\text{x}10^{-6}x^2 + 0.0017x + 19.605$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.71	20.02	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.08	19.46	19.39
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.57	21.02	20.89
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.09	20.58	20.40
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.03	20.56	20.33
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.65	20.21	19.93
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.33	20.95	20.61
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.49	19.37	18.71

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.49	19.41	18.70
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	20.40	21.46	20.63
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	13.73	14.47	13.88
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	19.65	20.77	19.87
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	14.52	15.38	14.68
188.58	Drift control - 20 μg dm^{-3} As	19.45	20.66	19.67
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.54	19.88	18.74
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.98	18.25	17.17
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	21.42	23.07	21.65
244.08	Drift control - 20 μg dm^{-3} As	20.22	21.84	20.44
296.78	Drift control - 20 μg dm^{-3} As	19.54	21.45	19.78

Table 4.36: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.005x + 19.626$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0118x + 19.273$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.78	19.93	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.65	19.76	19.81
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.72	20.81	20.83
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	20.24	20.23
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.09	20.05
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.79	19.76	19.70

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.52	20.46	20.36
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.38	19.06	18.86
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.02	19.65	19.45
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	22.80	22.34	22.10
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	15.35	15.01	14.85
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	22.27	21.74	21.51
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	16.99	16.56	16.38
188.58	Drift control - 20 μg dm^{-3} As	20.55	19.98	19.78
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.72	19.03	18.87
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.87	18.17	18.04
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	24.40	23.46	23.30
244.08	Drift control - 20 μg dm^{-3} As	21.23	20.37	20.26
296.78	Drift control - 20 μg dm^{-3} As	20.83	19.74	19.83

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

Calibration correlation coefficients of 0.9998, 1.0000 and 0.9999 together with detection limits of 1.927 μg dm^{-3} As, 1.195 μg dm^{-3} As and 1.814 μg dm^{-3} As were obtained respectively in the cases of using ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards. Tables 4.37 to 4.39 show the results of the analyses.

^{36}Ar and ^{37}Cl as internal standards yielded good results for matrices containing only nitric acid, but in the case of ^{35}Cl time drift correction resulted in too high values. When the matrix contained hydrochloric acid, the values obtained in the case of ^{36}Ar were slightly too low to be considered acceptable, but ^{35}Cl and ^{37}Cl as internal standards resulted in very poor quantitative values.

Table 4.37: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0181x + 19.889$) and second order equation used: ($y = 6\text{x}10^{-5}x^2 - 0.0363x + 20.843$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.35	20.29	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.00	19.00	18.83
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.01	20.21	20.11
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.13	20.47	20.46
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.58	20.03	20.09
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.12	19.67	19.80
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.09	20.87	21.08
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.40	17.79	18.24
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	13.79	16.06	16.47
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	13.53	15.88	16.29
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	8.56	10.13	10.38
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	11.98	14.28	14.63
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	8.10	9.73	9.96
188.58	Drift control - 20 μg dm^{-3} As	15.80	19.18	19.59
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.05	17.66	17.82
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	11.76	14.92	14.99
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	13.84	17.70	17.71
244.08	Drift control - 20 μg dm^{-3} As	15.52	20.06	19.95
296.78	Drift control - 20 μg dm^{-3} As	14.84	20.44	19.33

Table 4.38: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.299$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.712$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.04	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.53	20.53
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	23.17	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.60	24.38
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.73	23.47	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.75	26.93
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.99	4.22	5.44
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.25	1.81	2.37
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.07	1.58	2.11
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.96	1.46	1.96
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.97	1.50	2.05
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.93	1.48	2.03
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.32	16.99
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.44	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.21	2.30	3.02
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.07	2.11	2.71
244.08	Drift control - 20 μg dm^{-3} As	11.39	23.30	28.76
296.78	Drift control - 20 μg dm^{-3} As	8.87	23.63	20.22

Table 4.39: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 1.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0107x + 19.866$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0338x + 21.085$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	20.40	20.06
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.20	19.88	19.67
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.86	20.65	20.55
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.82	20.70	20.70
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.23	20.16	20.27
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.60	19.58	19.78
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.25	20.35	20.65
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.46	15.77	16.35
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.34	8.03	8.34
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	4.88	5.36	5.57
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	2.51	2.77	2.88
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	2.83	3.14	3.26
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	1.81	2.01	2.09
188.58	Drift control - 20 μg dm^{-3} As	16.74	18.76	19.46
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.72	15.66	16.10
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	6.50	7.45	7.63
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	5.06	5.83	5.95
244.08	Drift control - 20 μg dm^{-3} As	17.73	20.55	20.86
296.78	Drift control - 20 μg dm^{-3} As	16.97	20.34	19.71

4.5.7 *Effect of using molecular (mass 75 / mass 77) corrections in a 2.00% v/v HCl matrix on the quantitative determination of arsenic*

No internal standard

In this section the calculated correction factor of 3.199 for a solution of 2.00% v/v HCl was applied. In the case of no internal standard a correlation coefficient of 1.0000 was obtained for the calibration curve and the detection limit was calculated to be 1.686 μg dm^{-3} As. Table 4.40 show the values obtained after quantitative analyses.

From the table it can be seen that values of approximately 20 μg dm^{-3} were obtained when the sample matrix consisted of only nitric acid. Although this correction procedure proved to yield correct values of near to 20 μg dm^{-3} in some of the cases where hydrochloric acid was present in the matrix, it did not prove to be successful for the matrices of 1.00% v/v to 2.00% v/v HCl and (1.00% v/v HNO_3 + 1.00% v/v HCl).

Table 4.40: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0087x + 20.255$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0143x + 19.962$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.58	19.94	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.30	19.35
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.11	20.33	20.36
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.43	20.57	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.12	20.11
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.50	19.47
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.18	20.14
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.67	19.23	19.14
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.77	19.27	19.18

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.32	21.57	21.47
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	17.93	16.54	16.47
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	25.13	23.10	23.02
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	21.06	19.30	19.24
188.58	Drift control - 20 μg dm^{-3} As	21.93	20.03	19.98
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	20.57	18.56	18.58
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	19.92	17.92	17.96
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	25.19	22.59	22.67
244.08	Drift control - 20 μg dm^{-3} As	22.61	20.21	20.31
296.78	Drift control - 20 μg dm^{-3} As	22.63	19.82	20.16

^{45}Sc, ^{89}Y and ^{139}La as internal standards

Calibration curves with these three isotopes as internal standards yielded correlation coefficients of 1.0000 and detection limits of 1.738 μg dm^{-3} As, 1.696 μg dm^{-3} As and 1.688 μg dm^{-3} As respectively. The results of the quantitative analyses when using these internal standards are shown in tables 4.41 to 4.43.

All three the internal standards proved to be successful when only nitric acid where present in the matrix of the 20 μg dm^{-3} arsenic sample. With hydrochloric acid present in solution, analyses with all three internal standards resulted in values slightly deviating from the true value of 20 μg dm^{-3}. ^{139}La as internal standard yielded good values especially at low concentrations of hydrochloric acid.

Table 4.41: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0082x + 21.068$) and second order equation used: ($y = 8\text{x}10^{-5}x^2 - 0.0346x + 22.456$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.75	19.08	18.75
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.93	18.34	18.13
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.23	19.65	19.55
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	19.57	19.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	19.37	19.48
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.62	19.23	19.45
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.00	20.32
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.61	17.70	18.39
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	17.74	17.88	18.60
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	19.81	20.04	20.86
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	15.03	15.25	15.88
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	20.46	20.81	21.68
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	17.05	17.40	18.11
188.58	Drift control - 20 μg dm^{-3} As	18.54	18.99	19.75
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	16.99	17.63	18.15
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.33	17.01	17.44
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	20.94	21.88	22.35
244.08	Drift control - 20 μg dm^{-3} As	18.73	19.65	19.96
296.78	Drift control - 20 μg dm^{-3} As	18.32	19.66	19.05

Table 4.42: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0006x + 19.666$) and second order equation used: ($y = -6\text{x}10^{-6}x^2 + 0.0025x + 19.564$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.70	20.01	20.04
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.08	19.37	19.39
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.56	20.88	20.89
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.38	20.38
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.03	20.32	20.31
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.64	19.93	19.91
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.32	20.61	20.59
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.71	18.95	18.91
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.79	20.03	19.98
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.11	23.39	23.34
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	17.66	17.87	17.82
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	24.81	25.10	25.04
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	20.84	21.08	21.03
188.58	Drift control - 20 μg dm^{-3} As	19.52	19.74	19.70
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.83	19.02	19.00
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.56	18.75	18.73
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	24.46	24.70	24.68
244.08	Drift control - 20 μg dm^{-3} As	20.26	20.46	20.45
296.78	Drift control - 20 μg dm^{-3} As	19.60	19.76	19.82

Table 4.43: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0053x + 19.615$) and second order equation used: ($y = -2\text{x}10^{-6}x^2 + 0.0127x + 19.230$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	19.92	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.64	19.75	19.80
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.72	20.79	20.81
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.19	20.22	20.20
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.07	20.02
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.79	19.75	19.66
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.52	20.43	20.32
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.61	19.26	19.01
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.43	21.00	20.72
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	25.84	25.27	24.93
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	19.76	19.29	19.02
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	28.13	27.40	27.01
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	24.42	23.75	23.41
188.58	Drift control - 20 μg dm^{-3} As	20.63	20.02	19.73
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.03	19.28	19.02
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	20.63	19.82	19.57
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	27.87	26.73	26.41
244.08	Drift control - 20 μg dm^{-3} As	21.28	20.36	20.13
296.78	Drift control - 20 μg dm^{-3} As	20.91	19.74	19.69

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

With ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards correlation coefficients of 0.9998, 1.0000 and 0.9999 were obtained for the calibration curves. Detection limits were calculated to be 1.913 μg dm^{-3} As, 1.180 μg dm^{-3} As and 1.802 μg dm^{-3} As respectively. Tables 4.44 to 4.46 show the results of the quantitative analyses performed with these isotopes as internal standards.

Acceptable results were obtained when the sample did not contain hydrochloric acid, but for ^{35}Cl drift correction resulted in too high values. The two chlorine isotopes as internal standards did not result in acceptable values. ^{36}Ar as internal standard resulted in values slightly below the correct value of 20 μg dm^{-3}.

Table 4.44: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.018x + 19.877$) and second order equation used: ($y = 5\text{x}10^{-5}x^2 - 0.0356x + 20.807$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.34	20.28	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.99	19.00	18.85
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.00	20.20	20.13
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.11	20.46	20.48
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.57	20.02	20.12
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.10	19.66	19.84
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.08	20.86	21.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.58	18.00	18.61
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	14.79	17.22	17.83
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	15.39	18.05	18.71
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	11.15	13.19	13.68
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	15.24	18.16	18.85

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	11.81	14.19	14.74
188.58	Drift control - 20 μg dm^{-3} As	15.85	19.23	19.97
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.26	17.92	18.53
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	12.89	16.34	16.86
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	15.87	20.27	20.87
244.08	Drift control - 20 μg dm^{-3} As	15.54	20.07	20.58
296.78	Drift control - 20 μg dm^{-3} As	14.88	20.47	20.32

Table 4.45: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.294$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.708$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.54	20.54
59.10	Drift control - 20 μg dm^{-3} As	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 0.10% v/v HNO_3	20.20	23.17	23.31
73.68	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.20	23.61	24.38
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.72	23.47	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.75	26.94
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.98	4.20	5.42
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.24	1.79	2.34
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.05	1.56	2.08
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.94	1.43	1.93

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.95	1.47	2.01
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.91	1.45	1.99
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.33	17.00
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.44	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.20	2.28	2.99
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.06	2.09	2.67
244.08	Drift control - 20 μg dm^{-3} As	11.40	23.33	28.79
296.78	Drift control - 20 μg dm^{-3} As	8.88	23.66	20.24

Table 4.46: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.00% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0104x + 19.855$) and second order equation used: ($y = 7x10^{-5}x^2 - 0.0332x + 21.050$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	20.38	20.06
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.19	19.87	19.67
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.85	20.64	20.54
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.81	20.67	20.69
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.23	20.14	20.26
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.59	19.56	19.76
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.24	20.32	20.62
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.62	15.92	16.49
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.82	8.55	8.86

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	5.47	6.00	6.22
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.13	3.45	3.58
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	3.46	3.84	3.98
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	2.44	2.71	2.81
188.58	Drift control - 20 μg dm^{-3} As	16.79	18.77	19.44
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.92	15.85	16.25
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.07	8.08	8.25
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	5.72	6.57	6.68
244.08	Drift control - 20 μg dm^{-3} As	17.76	20.52	20.76
296.78	Drift control - 20 μg dm^{-3} As	17.02	20.31	19.61

4.5.8 Effect of using molecular (mass 75 / mass 77) corrections in a 2.50% v/v HCl matrix on the quantitative determination of arsenic

No internal standard

A correction factor of 3.169 was obtained for a solution containing 2.50% v/v HCl. With no internal standard being used, a correlation coefficient of 1.0000 was obtained together with a detection limit of 1.678 μg dm^{-3} As. Results are listed in table 4.47.

Samples containing only 20 μg dm^{-3} As and nitric acid yielded acceptable values. After drift correction was applied acceptable values for the samples containing HCl were obtained when the concentration of the hydrochloric acid was low.

Table 4.47: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0089x + 20.247$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0149x + 19.931$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.57	19.93	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.29	19.35
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.11	20.32	20.35
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.42	20.56	20.57
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.11	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.49	19.45
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.21	20.17	20.12
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.84	19.38	19.26
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.75	20.15	20.03
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	25.27	23.34	23.20
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	20.78	19.14	19.03
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	28.85	26.49	26.34
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	25.60	23.44	23.32
188.58	Drift control - 20 μg dm^{-3} As	21.99	20.06	19.97
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.80	18.74	18.71
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	21.14	18.98	18.97
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	27.42	24.55	24.56
244.08	Drift control - 20 μg dm^{-3} As	22.65	20.20	20.24
296.78	Drift control - 20 μg dm^{-3} As	22.69	19.83	20.09

^{45}Sc, ^{89}Y and ^{139}La as internal standards

With these three isotopes as internal standards correlation coefficients of the calibration curves were all 1.0000 and the detection limits were 1.730 μg dm^{-3} As, 1.687 μg dm^{-3} As and 1.680 μg dm^{-3} As respectively. Tables 4.48 to 4.50 show the results of quantitative analyses with these three internal standards.

Samples prepared from 20 μg dm^{-3} As and various concentrations of nitric acid yielded acceptable values in the cases of ^{45}Sc, ^{89}Y and ^{139}La as internal standards. For samples containing hydrochloric acid, none of the three internal standards yielded acceptable values over the whole range of hydrochloric acid concentrations.

Table 4.48: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0053x + 19.889$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0108x + 20.180$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.75	20.10	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.93	19.30	19.24
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.22	20.66	20.62
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.07	20.55	20.53
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.81	20.32	20.33
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.62	20.16	20.19
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.34	20.95	20.99
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.75	18.56	18.64
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.56	19.44	19.53
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	21.46	22.52	22.62
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	17.40	18.30	18.37

Time difference (minutes)	**Sample name**	[As] (μg dm^{-3})	**Corrected with first order drift curve** (μ**g dm**$^{-3}$)	**Corrected with second order drift curve** (μ**g dm**$^{-3}$)
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	23.47	24.73	24.81
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	20.70	21.86	21.92
188.58	Drift control - 20 μg dm^{-3} As	18.59	19.68	19.72
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	17.17	18.34	18.29
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	17.31	18.53	18.46
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	22.79	24.44	24.31
244.08	Drift control - 20 μg dm^{-3} As	18.76	20.18	20.03
296.78	Drift control - 20 μg dm^{-3} As	18.36	20.05	19.60

Table 4.49: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0008x + 19.658$) and second order equation used: ($y = -7\text{x}10^{-6}x^2 + 0.0031x + 19.535$)

Time difference (minutes)	**Sample name**	[As] (μg dm^{-3})	**Corrected with first order drift curve** (μ**g dm**$^{-3}$)	**Corrected with second order drift curve** (μ**g dm**$^{-3}$)
44.57	Drift control - 20 μg dm^{-3} As	19.69	20.00	18.88
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.07	19.36	18.10
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.56	20.87	19.31
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.07	20.37	18.67
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.02	20.31	18.44
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.64	19.91	17.91
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.32	20.60	18.36
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.87	19.09	15.94
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.71	20.95	17.34

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	25.04	25.32	20.79
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	20.46	20.67	16.84
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	28.48	28.77	23.24
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	25.34	25.59	20.51
188.58	Drift control - 20 μg dm^{-3} As	19.58	19.76	15.68
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.04	19.19	14.75
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	19.69	19.84	15.13
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	26.63	26.83	20.31
244.08	Drift control - 20 μg dm^{-3} As	20.29	20.44	15.34
296.78	Drift control - 20 μg dm^{-3} As	19.65	19.75	14.11

Table 4.50: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = 0.0056x + 19.607$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0133x + 19.200$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	19.91	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.64	19.74	19.80
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.71	20.78	20.80
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.18	20.20	20.19
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.06	20.01
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.78	19.72	19.64
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.52	20.41	20.29

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.78	19.39	19.12
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	22.44	21.95	21.63
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	28.00	27.34	26.93
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	22.89	22.30	21.96
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	32.29	31.40	30.91
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	29.71	28.83	28.38
188.58	Drift control - 20 μg dm^{-3} As	20.69	20.02	19.71
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.25	19.43	19.14
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	21.88	20.96	20.65
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	30.35	29.01	28.61
244.08	Drift control - 20 μg dm^{-3} As	21.31	20.32	20.06
296.78	Drift control - 20 μg dm^{-3} As	20.96	19.71	19.60

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards resulted in correlation coefficients of 0.9998, 1.0000 and 0.9999 together with detection limits of 1.903 μg dm^{-3} As, 1.170 μg dm^{-3} As and 1.793 μg dm^{-3} As respectively. Tables 4.51 to 4.53 show the results of the quantitative analyses when using these three isotopes as internal standards.

HNO_3 matrices resulted in acceptable values for ^{36}Ar and ^{37}Cl as internal standards, but time drift corrections resulted in too high values in the case of ^{35}Cl. ^{35}Cl and ^{37}Cl as internal standards did not result in acceptable values for samples containing HCl in the matrix. In the case of ^{36}Ar the results were generally too low.

Table 4.51: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0178x + 19.870$) and second order equation used: ($y = 5\times10^{-5}x^2 - 0.0352x + 20.781$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.34	20.27	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.99	18.99	18.84
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	18.99	20.18	20.12
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.10	20.44	20.47
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.56	20.01	20.11
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.09	19.64	19.82
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.07	20.84	21.11
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.71	18.13	18.73
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	15.51	18.03	18.65
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	16.71	19.58	20.28
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	13.00	15.34	15.90
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	17.55	20.89	21.66
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	14.46	17.34	17.99
188.58	Drift control - 20 μg dm^{-3} As	15.88	19.24	19.95
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.41	18.07	18.65
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	13.70	17.32	17.84
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	17.31	22.06	22.66
244.08	Drift control - 20 μg dm^{-3} As	15.55	20.03	20.51
296.78	Drift control - 20 μg dm^{-3} As	14.91	20.44	20.23

Table 4.52: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.290$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.705$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.25
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.54	20.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.19	23.18	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.61	24.39
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.72	23.48	24.90
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.76	26.94
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.97	4.19	5.41
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.23	1.77	2.33
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.04	1.54	2.05
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.93	1.41	1.90
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.94	1.45	1.98
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.90	1.43	1.96
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.33	17.00
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.43	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.19	2.27	2.98
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.05	2.07	2.65
244.08	Drift control - 20 μg dm^{-3} As	11.40	23.35	28.81
296.78	Drift control - 20 μg dm^{-3} As	8.88	23.69	20.26

Table 4.53: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at 2.50% v/v HCl. Results are also shown for time drift corrected values. First order equation used: ($y = -0.0103x + 19.846$) and second order equation used: ($y = 7x10^{-5}x^2 - 0.0327x + 21.025$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	20.38	20.05
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.19	19.87	19.66
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.84	20.63	20.53
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.80	20.67	20.67
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.22	20.14	20.24
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.58	19.55	19.73
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.24	20.31	20.59
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.74	16.04	16.58
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	8.16	8.92	9.23
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	5.89	6.46	6.68
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.57	3.93	4.07
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	3.92	4.34	4.49
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	2.89	3.21	3.32
188.58	Drift control - 20 μg dm^{-3} As	16.83	18.80	19.41
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.06	16.00	16.34
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.47	8.54	8.68
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	6.19	7.10	7.19
244.08	Drift control - 20 μg dm^{-3} As	17.79	20.52	20.66
296.78	Drift control - 20 μg dm^{-3} As	17.06	20.32	19.51

4.5.9 *Effect of using molecular (mass 75 / mass 77) corrections in a (0.10% v/v HNO_3 + 0.10% v/v HCl) matrix on the quantitative determination of arsenic*

No internal standard

A solution containing 0.10% v/v of nitric acid and 0.10% v/v hydrochloric acid resulted in a correction factor of 3.190. The calibration curve that was constructed, gave a correlation coefficient of 1.0000 and a detection limit of 1.683 μg dm^{-3} As was calculated. Table 4.54 shows the results of the quantitative analyses that were performed.

Nitric acid as sample matrix did not prove to be a problem and acceptable results were obtained. Reasonable results were obtained for samples containing low concentrations of hydrochloric acid.

Table 4.54: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0088x + 20.253$) and second order equation used: ($y = -2\text{x}10^{-5}x^2 + 0.0145x + 19.952$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.58	19.93	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.29	19.35
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.11	20.33	20.36
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.43	20.56	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.11	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.49	19.46
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.18	20.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.72	19.27	19.17
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.07	19.53	19.44
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.91	22.10	22.00
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	18.80	17.33	17.25

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	26.26	24.13	24.04
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	22.45	20.56	20.49
188.58	Drift control - 20 μg dm^{-3} As	21.95	20.03	19.98
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.64	18.61	18.62
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	20.29	18.24	18.27
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	25.87	23.18	23.25
244.08	Drift control - 20 μg dm^{-3} As	22.62	20.20	20.29
296.78	Drift control - 20 μg dm^{-3} As	22.65	19.81	20.14

^{45}Sc, ^{89}Y and ^{139}La as internal standards

Calibration curves that were constructed with ^{45}Sc, ^{89}Y and ^{139}La as internal standards resulted in correlation coefficients of 1.0000 and detection limits of 1.736 μg dm^{-3} As, 1.693 μg dm^{-3} As and 1.686 μg dm^{-3} As respectively. The results are listed in tables 4.55 to 4.57.

Values of approximately 20 μg dm^{-3} arsenic were obtained in the case of samples with matrices of only nitric acid. In the cases of all three the internal standards, acceptable results were obtained when the hydrochloric acid in the sample solution was present at a low concentration.

Table 4.55: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0054x + 19.894$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0112x + 20.198$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.75	20.10	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.93	19.30	19.25
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.22	20.66	20.63

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.56	20.55
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.33	20.34
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.62	20.17	20.21
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.96	21.01
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.65	18.46	18.57
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	17.99	18.85	18.97
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	20.32	21.34	21.46
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	15.76	16.58	16.68
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	21.38	22.54	22.67
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	18.16	19.20	19.29
188.58	Drift control - 20 μg dm^{-3} As	18.55	19.66	19.74
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	17.04	18.22	18.22
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.63	17.82	17.80
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	21.51	23.09	23.04
244.08	Drift control - 20 μg dm^{-3} As	18.74	20.18	20.09
296.78	Drift control - 20 μg dm^{-3} As	18.33	20.04	19.67

Table 4.56: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0006x + 19.664$) and second order equation used: ($y = -6x10^{-6}x^2 + 0.0027x + 19.555$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.70	20.01	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.08	19.37	19.39
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.56	20.88	20.88
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.38	20.38
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.02	20.32	20.31
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.64	19.93	19.90
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.32	20.62	20.58
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.76	19.00	18.94
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.07	20.32	20.25
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.70	23.99	23.91
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	18.51	18.74	18.67
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	25.93	26.23	26.13
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	22.21	22.47	22.38
188.58	Drift control - 20 μg dm^{-3} As	19.54	19.76	19.69
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.89	19.09	19.03
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.91	19.10	19.04
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	25.12	25.37	25.30
244.08	Drift control - 20 μg dm^{-3} As	20.27	20.47	20.42
296.78	Drift control - 20 μg dm^{-3} As	19.62	19.77	19.79

Table 4.57: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0054x + 19.612$) and second order equation used: ($y = -2\times10^{-5}x^2 + 0.0129x + 19.221$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	19.92	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.64	19.75	19.80
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.72	20.79	20.81
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.19	20.22	20.20
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.07	20.02
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.79	19.74	19.66
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.52	20.43	20.31
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.66	19.29	19.04
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.74	21.29	21.00
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	26.50	25.91	25.54
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	20.72	20.21	19.92
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	29.40	28.63	28.20
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	26.04	25.31	24.93
188.58	Drift control - 20 μg dm^{-3} As	20.65	20.02	19.72
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.10	19.32	19.06
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	21.01	20.17	19.90
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	28.63	27.42	27.08
244.08	Drift control - 20 μg dm^{-3} As	21.29	20.34	20.11
296.78	Drift control - 20 μg dm^{-3} As	20.93	19.73	19.66

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

The calibration curves constructed with these three internal standards resulted in correlation coefficients of 0.9998, 1.0000 and 0.9999 respectively. Detection limits were calculated to be 1.910 μg dm^{-3} As, 1.177 μg dm^{-3} As and 1.799 μg dm^{-3} As. The results of the quantitative analyses are shown in tables 4.58 to 4.60.

For nitric acid samples acceptable results were obtained, but from table 4.59 it can be seen that time drift procedures resulted in too high values for ^{35}Cl as internal standard. With samples containing hydrochloric acid in the matrix the two chlorine isotopes as internal standards did not result in acceptable values. In the case of ^{36}Ar the obtained values are generally just slightly below 20 μg dm^{-3}.

Table 4.58: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0179x + 19.875$) and second order equation used: ($y = 5\text{x}10^{-5}x^2 - 0.0355x + 20.799$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.34	20.28	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.99	18.99	18.85
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.00	20.19	20.13
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.11	20.45	20.48
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.57	20.01	20.12
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.10	19.65	19.83
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.08	20.85	21.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.62	18.03	18.65
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	15.01	17.46	18.08
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	15.79	18.51	19.20

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	11.72	13.84	14.36
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	15.94	18.98	19.72
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	12.62	15.15	15.74
188.58	Drift control - 20 μg dm^{-3} As	15.86	19.22	19.97
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.31	17.95	18.57
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	13.14	16.63	17.17
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	16.31	20.81	21.43
244.08	Drift control - 20 μg dm^{-3} As	15.54	20.05	20.57
296.78	Drift control - 20 μg dm^{-3} As	14.89	20.44	20.30

Table 4.59: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.293$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.707$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.54	20.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	23.17	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.61	24.39
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.72	23.48	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.76	26.94
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.97	4.20	5.41

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.23	1.78	2.34
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.05	1.55	2.07
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.94	1.42	1.92
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.95	1.47	2.00
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.91	1.44	1.98
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.33	17.00
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.44	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.20	2.28	2.99
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.06	2.08	2.67
244.08	Drift control - 20 μg dm^{-3} As	11.40	23.33	28.79
296.78	Drift control - 20 μg dm^{-3} As	8.88	23.67	20.24

Table 4.60: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.10% v/v HNO_3 + 0.10% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0104x + 19.852$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0330x + 21.043$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	21.49	20.05
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.19	20.96	19.66
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.85	21.77	20.53
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.81	21.81	20.68
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.23	21.26	20.25
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.59	20.64	19.74

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.24	21.46	20.60
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.66	16.88	16.51
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.92	9.16	8.97
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	5.59	6.50	6.36
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.26	3.81	3.73
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	3.60	4.22	4.13
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	2.58	3.03	2.97
188.58	Drift control - 20 μg dm^{-3} As	16.80	19.90	19.42
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.96	16.86	16.26
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.19	8.72	8.38
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	5.86	7.14	6.83
244.08	Drift control - 20 μg dm^{-3} As	17.77	21.79	20.71
296.78	Drift control - 20 μg dm^{-3} As	17.04	21.61	19.56

4.5.10 Effect of using molecular (mass 75 / mass 77) corrections in a (0.50% v/v HNO_3 + 0.50% v/v HCl) matrix on the quantitative determination of arsenic

No internal standard

A correction factor of 3.189 for the solution of (0.50% v/v HNO_3 + 0.50% v/v HCl) was calculated and used in the processing of the results in this section. The constructed calibration curve showed a correlation coefficient of 1.0000 and the detection limit was calculated to be 1.683 μg dm^{-3} As. The results of the quantitative analyses are shown in table 4.61.

Matrices of only nitric acid resulted in acceptable values of approximately 20 μg dm^{-3} arsenic. With hydrochloric acid present at low concentration in solution the correction procedure proved to yield acceptable results.

Table 4.61: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO_3 + 0.50% v/v HCl). Results also shown for time drift corrected values. First order equation used: ($y = 0.0088x + 20.252$) and second order equation used: ($y = -2x10^{-5}x^2 + 0.0145x + 19.952$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.58	19.93	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.29	19.35
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.11	20.33	20.36
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.43	20.57	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.12	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.43	19.49	19.46
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.18	20.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.72	19.27	19.18
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.08	19.55	19.45
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.94	22.13	22.02
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	18.84	17.36	17.29
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	26.31	24.18	24.08
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	22.51	20.62	20.54
188.58	Drift control - 20 μg dm^{-3} As	21.95	20.03	19.98
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.65	18.61	18.62
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	20.31	18.25	18.28
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	25.90	23.21	23.28
244.08	Drift control - 20 μg dm^{-3} As	22.62	20.20	20.29
296.78	Drift control - 20 μg dm^{-3} As	22.65	19.81	20.14

^{45}Sc, ^{89}Y and ^{139}La as internal standards

With ^{45}Sc, ^{89}Y and ^{139}La as internal standards the calibration curves yielded correlation coefficients of 1.0000 and detection limits were calculated at 1.736 μg dm^{-3} As, 1.693 μg dm^{-3} As and 1.686 μg dm^{-3} As respectively. Tables 4.62 to 4.64 show the values obtained after quantitative analyses.

Samples containing only nitric acid as matrix yielded values of approximately 20 μg dm^{-3} for all three internal standards. None of the three internal standards resulted in acceptable values for all concentrations of hydrochloric acid present in solution.

Table 4.62: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO_3 + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0054x + 19.894$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0112x + 20.198$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.75	20.10	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.93	19.30	19.25
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.22	20.66	20.63
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.56	20.55
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.33	20.34
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.62	20.17	20.21
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.96	21.01
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.65	18.46	18.57
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.00	18.86	18.98
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	20.34	21.36	21.49
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	15.79	16.61	16.71
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	21.42	22.58	22.71

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	18.21	19.25	19.34
188.58	Drift control - 20 μg dm^{-3} As	18.55	19.66	19.74
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	17.04	18.22	18.23
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.64	17.83	17.81
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	21.53	23.12	23.06
244.08	Drift control - 20 μg dm^{-3} As	18.74	20.18	20.09
296.78	Drift control - 20 μg dm^{-3} As	18.33	20.04	19.67

Table 4.63: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO_3 + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0006x + 19.664$) and second order equation used: ($y = -6\text{x}10^{-6}x^2 + 0.0027x + 19.555$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.70	20.01	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.08	19.37	19.39
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.56	20.88	20.88
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.08	20.38	20.38
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.02	20.32	20.31
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.64	19.93	19.90
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.32	20.62	20.58
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.77	19.00	18.94
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	20.08	20.33	20.26
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	23.73	24.02	23.93

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	18.55	18.77	18.70
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	25.97	26.28	26.18
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	22.27	22.53	22.44
188.58	Drift control - 20 μg dm^{-3} As	19.54	19.76	19.69
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	18.90	19.09	19.03
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	18.92	19.11	19.05
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	25.15	25.40	25.33
244.08	Drift control - 20 μg dm^{-3} As	20.27	20.47	20.42
296.78	Drift control - 20 μg dm^{-3} As	19.62	19.77	19.79

Table 4.64: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO$_3$ + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0054x + 19.612$) and second order equation used: ($y = -2\text{x}10^{-6}x^2 + 0.0129x + 19.221$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.77	19.92	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO$_3$	19.64	19.75	19.80
59.10	20 μg dm^{-3} As in 0.50% v/v HNO$_3$	20.72	20.79	20.81
66.42	20 μg dm^{-3} As in 1.00% v/v HNO$_3$	20.19	20.22	20.20
73.68	20 μg dm^{-3} As in 1.50% v/v HNO$_3$	20.08	20.07	20.02
80.95	20 μg dm^{-3} As in 2.00% v/v HNO$_3$	19.79	19.74	19.66
88.22	20 μg dm^{-3} As in 2.50% v/v HNO$_3$	20.52	20.43	20.31
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.66	19.30	19.04

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Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	21.75	21.30	21.01
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	26.53	25.93	25.57
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	20.76	20.25	19.96
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	29.45	28.68	28.26
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	26.11	25.37	24.99
188.58	Drift control - 20 μg dm^{-3} As	20.65	20.02	19.72
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.10	19.33	19.06
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	21.03	20.18	19.91
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	28.66	27.46	27.11
244.08	Drift control - 20 μg dm^{-3} As	21.29	20.34	20.11
296.78	Drift control - 20 μg dm^{-3} As	20.93	19.73	19.66

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

These three internal standards resulted in calibration curves with correlation coefficients of 0.9998, 1.0000 and 0.9999 respectively. The detection limits were calculated to be 1.910 μg dm^{-3} As, 1.177 μg dm^{-3} As and 1.799 μg dm^{-3} As. The values obtained after quantitative analyses can be seen in tables 4.65 to 4.67.

In the cases of ^{36}Ar and ^{37}Cl good results were obtained for samples containing no hydrochloric acid. In the case of ^{35}Cl drift correction procedures resulted in too high values. With hydrochloric acid present in solution and the chlorine isotopes as internal standards too low values were obtained. In the case of ^{36}Ar as internal standard the values obtained are generally below the accepted value of 20 μg dm^{-3}.

Table 4.65: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO_3 + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0179x + 19.875$) and second order equation used: ($y = 5\text{x}10^{-5}x^2 - 0.0355x + 20.798$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.34	20.28	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	17.99	18.99	18.85
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.00	20.19	20.13
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.11	20.45	20.48
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.57	20.01	20.12
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.10	19.65	19.83
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.08	20.85	21.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.62	18.04	18.65
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	15.02	17.47	18.09
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	15.81	18.53	19.22
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	11.74	13.87	14.39
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	15.97	19.02	19.75
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	12.66	15.19	15.78
188.58	Drift control - 20 μg dm^{-3} As	15.86	19.22	19.97
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	14.31	17.96	18.57
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	13.15	16.64	17.18
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	16.33	20.83	21.45
244.08	Drift control - 20 μg dm^{-3} As	15.54	20.05	20.57
296.78	Drift control - 20 μg dm^{-3} As	14.89	20.45	20.30

Table 4.66: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO$_3$ + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0431x + 20.293$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.707$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.03	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO$_3$	19.45	21.54	20.54
59.10	20 μg dm^{-3} As in 0.50% v/v HNO$_3$	20.31	22.89	22.42
66.42	20 μg dm^{-3} As in 1.00% v/v HNO$_3$	20.20	23.17	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO$_3$	20.20	23.61	24.39
80.95	20 μg dm^{-3} As in 2.00% v/v HNO$_3$	19.72	23.48	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO$_3$	20.41	24.76	26.94
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.97	4.20	5.41
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.23	1.78	2.34
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.05	1.55	2.07
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.94	1.42	1.92
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.95	1.47	2.00
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.91	1.44	1.98
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.33	17.00
220.02	20 μg dm^{-3} As in (0.10% v/v HNO$_3$ + 0.10% v/v HCl)	2.94	5.44	7.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO$_3$ + 0.50% v/v HCl)	1.20	2.28	2.99
234.78	20 μg dm^{-3} As in (1.00% v/v HNO$_3$ + 1.00% v/v HCl)	1.06	2.08	2.67
244.08	Drift control - 20 μg dm^{-3} As	11.40	23.33	28.79
296.78	Drift control - 20 μg dm^{-3} As	8.88	23.67	20.25

Table 4.67: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (0.50% v/v HNO_3 + 0.50% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0104x + 19.852$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0330x + 21.042$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	19.76	20.39	20.05
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.19	19.87	19.66
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.85	20.64	20.53
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.81	20.67	20.68
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.23	20.15	20.25
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.59	19.56	19.74
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.24	20.32	20.60
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.66	15.96	16.51
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.93	8.67	8.98
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	5.60	6.15	6.37
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	3.27	3.61	3.74
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	3.61	4.00	4.14
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	2.58	2.87	2.97
188.58	Drift control - 20 μg dm^{-3} As	16.81	18.79	19.42
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.97	15.90	16.27
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	7.20	8.23	8.39
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	5.87	6.74	6.84
244.08	Drift control - 20 μg dm^{-3} As	17.77	20.53	20.71
296.78	Drift control - 20 μg dm^{-3} As	17.04	20.32	19.57

4.5.11 Effect of using molecular (mass 75 / mass 77) corrections in a (1.00% v/v HNO_3 + 1.00% v/v HCl) matrix on the quantitative determination of arsenic

No internal standard

A correction factor of 3.252 was calculated from analysis of a solution containing (1.00% v/v HNO_3 + 1.00% v/v HCl). The calibration curve that was constructed resulted in a correlation coefficient of 1.0000 and a detection limit of 1.700 μg dm^{-3} As was calculated. Table 4.68 shows the results obtained.

With no hydrochloric acid present in solution, values of approximately 20 μg dm^{-3} arsenic were obtained. With hydrochloric acid present in solution the values obtained showed to be slightly less than 20 μg dm^{-3}.

Table 4.68: Results of quantitative determination of As using no internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0083x + 20.269$) and second order equation used: ($y = -1\text{x}10^{-5}x^2 + 0.0130x + 20.016$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	20.59	19.95	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.98	19.31	19.34
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	21.12	20.35	20.36
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	21.44	20.59	20.58
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	21.02	20.14	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	20.44	19.52	19.46
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	21.22	20.21	20.13
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	20.34	18.97	18.78
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.00	17.66	17.48
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	19.78	18.33	18.13

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	12.77	11.80	11.67
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	18.37	16.94	16.74
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	12.80	11.76	11.62
188.58	Drift control - 20 μg dm^{-3} As	21.82	19.98	19.73
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	20.16	18.25	18.00
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	17.72	15.99	15.78
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	21.13	19.02	18.77
244.08	Drift control - 20 μg dm^{-3} As	22.54	20.22	19.95
296.78	Drift control - 20 μg dm^{-3} As	22.52	19.81	19.59

^{45}Sc, ^{89}Y and ^{139}La as internal standards

Correlation coefficients of 1.0000 were obtained when using these three isotopes as internal standards. Detection limits of 1.753 μg dm^{-3} As, 1.711 μg dm^{-3} As and 1.704 μg dm^{-3} As were obtained respectively for the three internal standards. The results obtained can be seen in tables 4.69 to 4.71.

In the cases of nitric acid sample matrices all three internal standards resulted in acceptable values of approximately 20 μg dm^{-3}. Although none of the three internal standards yielded acceptable values over the whole concentration range of hydrochloric acid used in the sample matrices, ^{139}La yielded acceptable values when the hydrochloric acid was present at low concentrations.

Table 4.69: Results of quantitative determination of As using ^{45}Sc as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0058x + 19.909$) and second order equation used: ($y = 2\text{x}10^{-5}x^2 - 0.0124x + 20.256$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.76	20.12	20.02
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.94	19.32	19.26
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.24	20.69	20.66
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.09	20.58	20.59
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.82	20.35	20.38
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.63	20.20	20.26
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.35	20.99	21.07
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	17.34	18.18	18.36
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	16.24	17.06	17.23
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	16.83	17.71	17.90
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	10.73	11.32	11.44
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	14.99	15.86	16.02
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	10.41	11.03	11.15
188.58	Drift control - 20 μg dm^{-3} As	18.46	19.62	19.81
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	16.66	17.88	18.01
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	14.54	15.65	15.75
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	17.59	18.97	19.07
244.08	Drift control - 20 μg dm^{-3} As	18.69	20.21	20.29
296.78	Drift control - 20 μg dm^{-3} As	18.24	20.06	19.89

Table 4.70: Results of quantitative determination of As using ^{89}Y as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0002x + 19.680$) and second order equation used: ($y = -4\times10^{-6}x^2 + 0.0014x + 19.617$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.71	20.02	20.04
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.08	19.39	19.40
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.57	20.90	20.90
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.09	20.41	20.41
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.03	20.34	20.34
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.65	19.95	19.94
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.33	20.64	20.63
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	18.43	18.70	18.68
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	18.11	18.37	18.35
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	19.61	19.89	19.87
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	12.57	12.76	12.74
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	18.14	18.40	18.38
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	12.67	12.85	12.83
188.58	Drift control - 20 μg dm^{-3} As	19.43	19.71	19.69
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	18.46	18.72	18.71
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	16.52	16.75	16.75
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	20.53	20.81	20.81
244.08	Drift control - 20 μg dm^{-3} As	20.21	20.49	20.50
296.78	Drift control - 20 μg dm^{-3} As	19.52	19.77	19.83

Table 4.71: Results of quantitative determination of As using ^{139}La as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = 0.0049x + 19.630$) and second order equation used: ($y = -2x10^{-5}x^2 + 0.0115x + 19.285$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.78	19.93	20.03
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.65	19.76	19.82
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.73	20.81	20.84
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	20.25	20.24
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.08	20.09	20.06
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.80	19.77	19.71
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.53	20.46	20.38
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	19.31	19.00	18.82
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	19.61	19.26	19.08
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	21.91	21.48	21.27
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	14.06	13.76	13.63
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	20.56	20.08	19.89
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	14.82	14.45	14.31
188.58	Drift control - 20 μg dm^{-3} As	20.53	19.98	19.80
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	19.63	18.96	18.83
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	18.35	17.69	17.59
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	23.38	22.50	22.39
244.08	Drift control - 20 μg dm^{-3} As	21.22	20.38	20.30
296.78	Drift control - 20 μg dm^{-3} As	20.81	19.74	19.88

^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards

The correlation coefficients obtained were 0.9998, 1.0000 and 0.9999 when using ^{36}Ar, ^{35}Cl and ^{37}Cl as internal standards. The detection limits calculated for these three cases were 1.931 μg dm^{-3} As, 1.199 μg dm^{-3} As and 1.818 μg dm^{-3} As respectively. The results obtained from the quantitative analysis can be seen in tables 4.72 to 4.74.

With only nitric acid present in the sample matrix good results were obtained for ^{36}Ar and ^{37}Cl as internal standards. In the case of ^{35}Cl the time drift correction procedure resulted in too high values. With ^{35}Cl and ^{37}Cl as internal standards very poor values were obtained and with ^{36}Ar as internal standard the values obtained showed generally to be slightly less than 20 μg dm^{-3}.

Table 4.72: Results of quantitative determination of As using ^{36}Ar as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0182x + 19.892$) and second order equation used: ($y = 6x10^{-5}x^2 - 0.0365x + 20.854$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.36	20.29	20.01
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	18.01	19.01	18.83
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.02	20.21	20.12
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.13	20.48	20.47
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	18.58	20.03	20.10
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.12	19.67	19.81
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.09	20.88	21.10
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	15.35	17.74	18.19
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	13.50	15.73	16.14
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	12.99	15.25	15.65
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	7.80	9.24	9.48

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	11.02	13.15	13.48
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	7.01	8.43	8.64
188.58	Drift control - 20 μg dm^{-3} As	15.78	19.18	19.60
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.98	17.60	17.78
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	11.43	14.51	14.60
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	13.25	16.96	16.99
244.08	Drift control - 20 μg dm^{-3} As	15.51	20.08	19.99
296.78	Drift control - 20 μg dm^{-3} As	14.83	20.47	19.37

Table 4.73: Results of quantitative determination of As using ^{35}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0432x + 20.301$) and second order equation used: ($y = 0.0003x^2 - 0.1461x + 25.713$)

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
44.57	Drift control - 20 μg dm^{-3} As	20.04	21.81	20.24
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.45	21.54	20.53
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	20.31	22.89	22.41
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	20.20	23.18	23.31
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	20.20	23.60	24.37
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	19.73	23.48	24.89
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	20.41	24.76	26.93
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	2.99	4.23	5.44
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	1.26	1.82	2.38

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	1.07	1.59	2.11
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	0.97	1.47	1.97
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	0.97	1.51	2.06
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	0.94	1.49	2.04
188.58	Drift control - 20 μg dm^{-3} As	7.50	12.34	16.99
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	2.94	5.45	7.28
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	1.21	2.31	3.02
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	1.08	2.12	2.71
244.08	Drift control - 20 μg dm^{-3} As	11.39	23.35	28.75
296.78	Drift control - 20 μg dm^{-3} As	8.87	23.71	20.21

Table 4.74: Results of quantitative determination of As using ^{37}Cl as internal standard and the molecular correction factor (mass 75 / mass 77) at (1.00% v/v HNO_3 + 1.00% v/v HCl). Results are also shown for time drift corrected values. First order equation used: ($y = -0.0107x + 19.870$) and second order equation used: ($y = 7\text{x}10^{-5}x^2 - 0.0340x + 21.095$)

Time difference (minutes)	**Sample name**	**[As] (μg dm^{-3})**	**Corrected with first order drift curve (μg dm^{-3})**	**Corrected with second order drift curve (μg dm^{-3})**
44.57	Drift control - 20 μg dm^{-3} As	19.78	20.39	20.06
51.83	20 μg dm^{-3} As in 0.10% v/v HNO_3	19.20	19.88	19.67
59.10	20 μg dm^{-3} As in 0.50% v/v HNO_3	19.86	20.65	20.55
66.42	20 μg dm^{-3} As in 1.00% v/v HNO_3	19.82	20.69	20.71
73.68	20 μg dm^{-3} As in 1.50% v/v HNO_3	19.24	20.16	20.28
80.95	20 μg dm^{-3} As in 2.00% v/v HNO_3	18.60	19.58	19.79
88.22	20 μg dm^{-3} As in 2.50% v/v HNO_3	19.25	20.35	20.66

Time difference (minutes)	Sample name	[As] (μg dm^{-3})	Corrected with first order drift curve (μg dm^{-3})	Corrected with second order drift curve (μg dm^{-3})
142.48	20 μg dm^{-3} As in 0.10% v/v HCl	14.41	15.71	16.31
149.82	20 μg dm^{-3} As in 0.50% v/v HCl	7.19	7.88	8.19
157.18	20 μg dm^{-3} As in 1.00% v/v HCl	4.70	5.17	5.38
164.55	20 μg dm^{-3} As in 1.50% v/v HCl	2.33	2.57	2.68
171.92	20 μg dm^{-3} As in 2.00% v/v HCl	2.64	2.93	3.05
179.30	20 μg dm^{-3} As in 2.50% v/v HCl	1.62	1.81	1.88
188.58	Drift control - 20 μg dm^{-3} As	16.72	18.73	19.47
220.02	20 μg dm^{-3} As in (0.10% v/v HNO_3 + 0.10% v/v HCl)	13.66	15.59	16.06
227.40	20 μg dm^{-3} As in (0.50% v/v HNO_3 + 0.50% v/v HCl)	6.33	7.26	7.45
234.78	20 μg dm^{-3} As in (1.00% v/v HNO_3 + 1.00% v/v HCl)	4.87	5.61	5.74
244.08	Drift control - 20 μg dm^{-3} As	17.72	20.54	20.89
296.78	Drift control - 20 μg dm^{-3} As	16.96	20.31	19.75

4.6 Conclusion

It was shown that very good calibration curves together with detection limits that varied from 0.493 μg dm^{-3} to 1.939 μg dm^{-3} arsenic are attainable for the quantitative determination of mono-isotopic arsenic in acidic matrices.

As it is known that instrumental drift occurs with time in ICP-MS the extent thereof was measured and the results were adjusted accordingly. It was seen that correction for this drift phenomena resulted in accurate analytical results. Internal standards that resulted in acceptable analytical results were ^{45}Sc, ^{89}Y, ^{139}La and ^{36}Ar, while the use of ^{35}Cl and ^{37}Cl as internal standards did not always have the desired effect.

Nitric acid concentrations were varied from 0.10% v/v to 2.50% v/v and this caused no problems or interferences in quantitative analyses.

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The hydrochloric acid concentration in solution was varied from 0.10% v/v to 2.50% v/v. It was shown that correction procedures are necessary when chlorine is present in the matrix and arsenic has to be determined quantitatively. It was shown that the use of internal standards could not compensate for the chlorine interference on mono-isotopic arsenic at mass 75, as the values are not effected by only instrumental drift, but are the result of dimer formation.

Molecular correction factors were determined at different acid concentrations and the results were adjusted accordingly. The effects of the internal standards together with these correction factors on the arsenic determinations were also studied. Most of the correction factors compensated for the effect of the dimer formation at mass 75 for hydrochloric acid concentrations of less than 1.50% v/v. Under normal conditions the acid concentration of samples prepared for ICP-MS analysis do not exceed 1.00% v/v. For such samples the proposed dimer correction procedures together with instrumental drift monitoring proved to result in acceptable results. For samples with a hydrochloric acid content of more than 1.00% v/v the correction procedures do not compensate for the dimer formation adequately, effectively resulting in unacceptable values.