Chapter 5

LOWERING THE DETECTION LIMIT FOR ARSENIC: OUTLOOK FOR A NEW PRACTICAL QUANTITATION LIMIT

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5.1 Abstract

The practical quantitation limit (PQL) for arsenic, which is regulated under both the Safe Drinking Water Act and Clean Water Act of the United States, is currently orders of magnitude higher that its nonenforceable, health-based standard in the state of California. Analytical limitations are primarily due to interference by chloride, a natural constituent of drinking water. This interference can be overcome using high-resolution, inductively coupled plasma mass spectrometry (ICP-MS), which has a method detection limit (MDL) for arsenic of 29 ng L^{-1} in the presence of 35.5 mg L^{-1} chloride. Increasing chloride concentration (0–355 mg L^{-1}) resulted in a nonlinear increase in the arsenic signal. Hence, standard addition was used to test four water samples with unknown arsenic and chloride concentrations. The applicability of high resolution ICP-MS and other methods for trace arsenic analysis to water quality testing is discussed. Broader adoption of such advanced analytical methods could result in lowering of the PQL for arsenic in the future, with consequent downward pressure on reporting levels and even possibly on the arsenic maximum contaminant level.

5.2 Introduction

Exposure to arsenic (As) in drinking water is associated with increased risk of bladder, liver, kidney, and skin cancers (Goyer et al. 2001; Smith et al. 2002). To mitigate these risks, the United States Environmental Protection Agency (US EPA) revised the maximum contaminant level (MCL) for As in 2001. After considering possible standards ranging from 5–20 μg L^{-1}, the US EPA set the MCL for As at 10 μg L^{-1}. This rule will come into force in January 2006 (US EPA 2002c). States have the option to set their own regulatory standards at or below the federal MCL; the New Jersey standard is 5 μg L^{-1} (NJDEP 2004), and other states, such as California, are currently evaluating their state standards. These enforceable standards must be set as close to corresponding health-based standards as is feasible. The federal health standard, the maximum contaminant level goal (MCLG), is defined as the concentration of a drinking water contaminant at which there is no known or expected risk to health. The MCLG for As and all other carcinogens is set to zero because it is assumed that there is no threshold for cancer risk. In contrast, California's public health goal (PHG) for As is 0.004 μg L^{-1} based on an excess risk of 10^{-6} from lifetime water consumption of 2 L day^{-1}.

The major factors that determine whether a value for an MCL is feasible are analytical capabilities and cost of treatment. Since treatment costs can be difficult to estimate, analytical limitations can be convenient criteria for feasibility. Regulatory enforcement requires that routine measurements of the target contaminant be reliable. Thus, the US EPA establishes practical quantitation levels (PQLs), which are defined as the lowest analyte concentration that can be reliably measured within specified limits of precision and accuracy (typically 25–30%) during routine laboratory operation

conditions. It is to be expected that certain individual laboratories will be capable of detecting a given chemical contaminant at lower levels than the PQL, but these cannot be considered routine analyses.

Another analytical descriptor, the method detection limit (MDL), delimits the lowest analyte concentration that can be distinguished from a blank. The MDL is specific to a given method, and it may differ between laboratories or even within an individual laboratory due to variations in instrument response or operator capabilities. Although the PQL is usually defined based on an interlaboratory study, in the absence of such data the PQL is typically set to 5 times the average MDL (Eaton 1994).

For As, the PQL is nearly three orders of magnitude greater than California's PHG (Table 5.1). The national average MDL using transmission quadrupole ICP-MS is 1.4 $\mu g\ L^{-1}$. This value, although lower than the PQL, is still 350 times higher than the California PHG. The MDL for ICP-MS is limited by an interference derived from the presence of chloride (Cl) in the drinking water matrix. In the argon (Ar) plasma gas, an $ArCl^+$ dimer can be formed with mass 74.93 amu, which is very close to the As^+ mass, 74.92 amu. This interference, however, is not an absolute limit and can be circumvented with currently available technology.

This study illustrates the use of a commercially available high resolution ICP-MS instrument to detect As concentrations much lower than the PQL in the presence of Cl concentrations typical of drinking water. Several other analytical methods with low detection limits for As are also described to draw readers' attention to the variety of methods that may allow the PQL for As to be lowered in the future.

Table 5.1. Regulated water contaminants with practical quantitation limits higher than corresponding health goals.

Contaminant	MCL[a] ($\mu g\ L^{-1}$)	PQL[b] ($\mu g\ L^{-1}$)	MCLG[a] ($\mu g\ L^{-1}$)	PHG[c] ($\mu g\ L^{-1}$)
Arsenic	10	3	0	0.004
Cadmium	5	2	5	0.07
Thallium	2	2	0.5	0.1
Benzene	5	5	0	0.15
Benzo(a)pyrene	0.2	0.2	0	0.004
Dichloromethane	5	5	0	4
Heptachlor	0.4	0.4	0	0.008
Heptachlor epoxide	0.2	0.2	0	0.006
Hexachlorobenzene	1	1	0	0.03
Pentachlorophenol	1	1	0	0.4
Vinyl Chloride	2	2	0	0.05

a (US EPA 2002e)
b PQLs for inorganics are given in (US EPA 1999); PQLs for organics are from (US EPA 2005)
c (CAOEHHA 2004)

This issue of analytical constraints on the feasible level for the MCL is not limited to As. There are numerous examples of drinking water contaminants for which the current PQL is higher than the MCLG or California's PHG (Table 5.1). Despite these disparities between analytical and health standards, a given chemical contaminant may receive little attention if its concentration falls below the PQL. This paper seeks to point out that such practices ignore the rapid development of analytical capabilities, which could drive further re-evaluations of the PQL. Since the PQL is a moving target, reliance

on the PQL in defining a feasible MCL may leave enforceable standards open to future challenges. Arsenic is a particularly compelling case because the widespread publicity associated with recent changes in the drinking water standard may provide an incentive to improve analytical capabilities.

5.3 Materials and Methods

5.3.1 Calibration standards

All solutions were prepared in new polypropylene tubes that were acid washed in 5% nitric acid (Omnitrace). Arsenic calibration standards (SCP Science ICP Standard) ranged from 2.5 to 2500 ng L^{-1} and were prepared in 1% nitric acid. Analytical grade sodium chloride (Baker ULTREX) was added to some standards to achieve Cl concentrations ranging from 3.55 to 355 mg L^{-1}. All solutions were prepared gravimetrically.

5.3.2 Sample preparation

Three brands of bottled water and a tap water sample were analyzed for As. Bottled waters A and B were mountain spring waters from the U.S. and abroad, respectively, whereas bottled water C was purified tap water. Due to the unknown matrices (in particular, Cl concentrations) for all four of these water samples, the method of standard additions was used to determine As concentrations. Nitric acid was added to each sample to achieve 1% HNO_3, and samples were spiked with 0, 10, 25, 50, 100, and 250 ng L^{-1} As before analysis. The addition of HNO_3 and As resulted in dilution of the

samples by 10–15% for bottled water samples A–C, tap water samples were further diluted to a total dilution factor of 4.

5.3.3 Analytical method

Samples were run on a magnetic sector field ICP-MS instrument (Thermo Finnigan ELEMENT) using a microflow nebulizer (Elemental Scientific PFA-20) and a Peltier-cooled cyclonic spray chamber (Elemental Scientific PC3 SSI). The instrument was set on high resolution mode. Depending on instrument tuning conditions, this setting corresponded to a measured resolution (R) of 7900–10,000, where

$$R = \frac{mass}{\Delta peak_{(5\%\ \text{height})}}$$

Thus, a resolution of 10,000 provides a detection peak for As^+ (mass 75) that is 0.0075 amu wide at 5% of the maximum peak height. Since the As^+ and $ArCl^+$ peak masses differ by 0.01 amu, this resolution is sufficient to separate the two peaks, although some small degree of overlap remains. Further instrument operating conditions and data collection parameters are detailed in Table 5.2. The mass ranges corresponding to As^+ and $ArCl^+$ were scanned 200 times for each sample, and the average counts per second for each mass were calculated. Data were obtained by integrating 20% of the total peak width centered around the maximum average peak height. To correct for mass drift over time, a separate method, run alternately with the sample method, identified the $ArAr^+$ peak (mass 80) derived from the plasma gas. The instrument used the difference between the measured and expected peak masses for $ArAr^+$ to adjust the mass scan window such that the As^+ and $ArCl^+$ peaks remained centered.

Table 5.2. ICP-MS operating and data collection conditions.

Rf power (W)	1297
Plasma cool gas (L min^{-1})	15.1
Auxiliary gas (L min^{-1})	1.0
Sample gas (L min^{-1})	0.97
Sample flow rate (μL min^{-1})	35
Torch	Not shielded
Scan range (amu)	74.916-74.935
Sample time (s)	0.05
Samples per peak	40
Scan type	Electric
Peak search window (%)	100
Sample run time (min)	14

5.4 Results

5.4.1 Instrumental calibration and detection limits

An example of As^+ and $ArCl^+$ peak separation is shown in Figure 5.1. After quantifying such peaks, calibration curves were generated for standards with both 0 and 35.5 mg Cl L^{-1} (Figure 5.2). Due to the slight overlap between the As^+ and $ArCl^+$ signals, Cl does contribute to the overall signal attributed to As^+. Thus, the dependence of the As^+ signal on Cl concentration was examined with [As] = 250 ng L^{-1} and [Cl] varied from 3.55 to 355 mg L^{-1} (Figure 5.3). The upper limit of this range is below the secondary

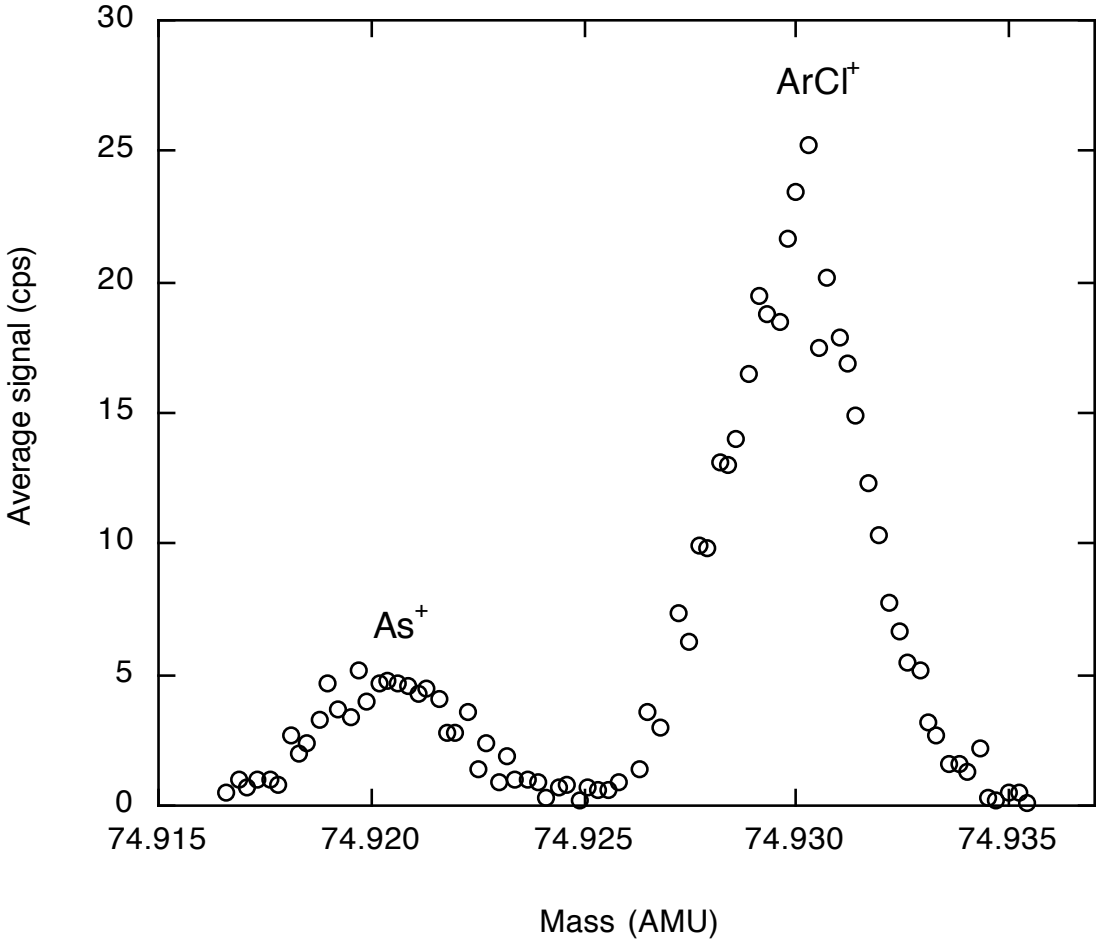

Figure 5.1. Peak separation for As^+ and $ArCl^+$. Conditions: [As] = 50 ng L^{-1}, [Cl] = 35.5 mg L^{-1}.

MCL for Cl (500 mg L^{-1}) but higher than would be expected in most drinking water samples. Over this [Cl] range, the signal attributed to As^+ increases with increasing [Cl], though not linearly. This phenomenon may be due to typical peak tailing behavior; peaks tail off exponentially at first, followed by a linear decrease at the tail ends. As the $ArCl^+$

peak gets larger and broader, the mass at which it overlaps with the As^+ peak may transition from the linearly decreasing region to the exponentially decreasing region of the $ArCl^+$ peak. For practical application, the threefold increase in As^+ signal as [Cl] is varied from 0 to 355 mg L^{-1} is not problematic, although it does indicate that samples with unknown chloride levels should be analyzed using the method of standard additions.

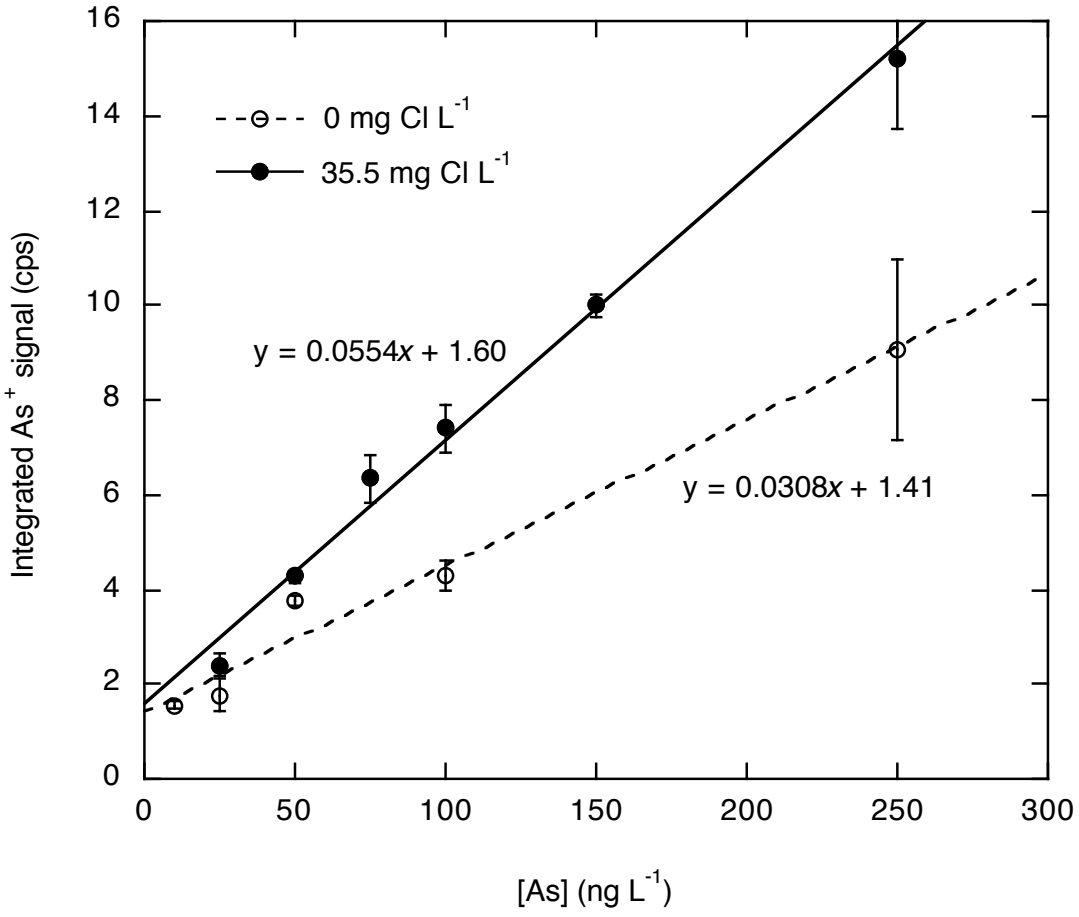

Figure 5.2. Standard As calibration curves. Standards were run in triplicate; error bars correspond to one standard deviation.

The instrumental detection limit, defined as 3 standard deviations above the mean blank signal (n = 7), was 13 ng L^{-1}. With optimal instrument performance, As

concentrations as low as 5 ng L^{-1} could be distinguished from low levels of $ArCl^+$. The MDL, defined as the amount of As that can be processed through the entire method and still produce a signal large enough to be detected in 99% of trials, was calculated to be 29 ng L^{-1}.

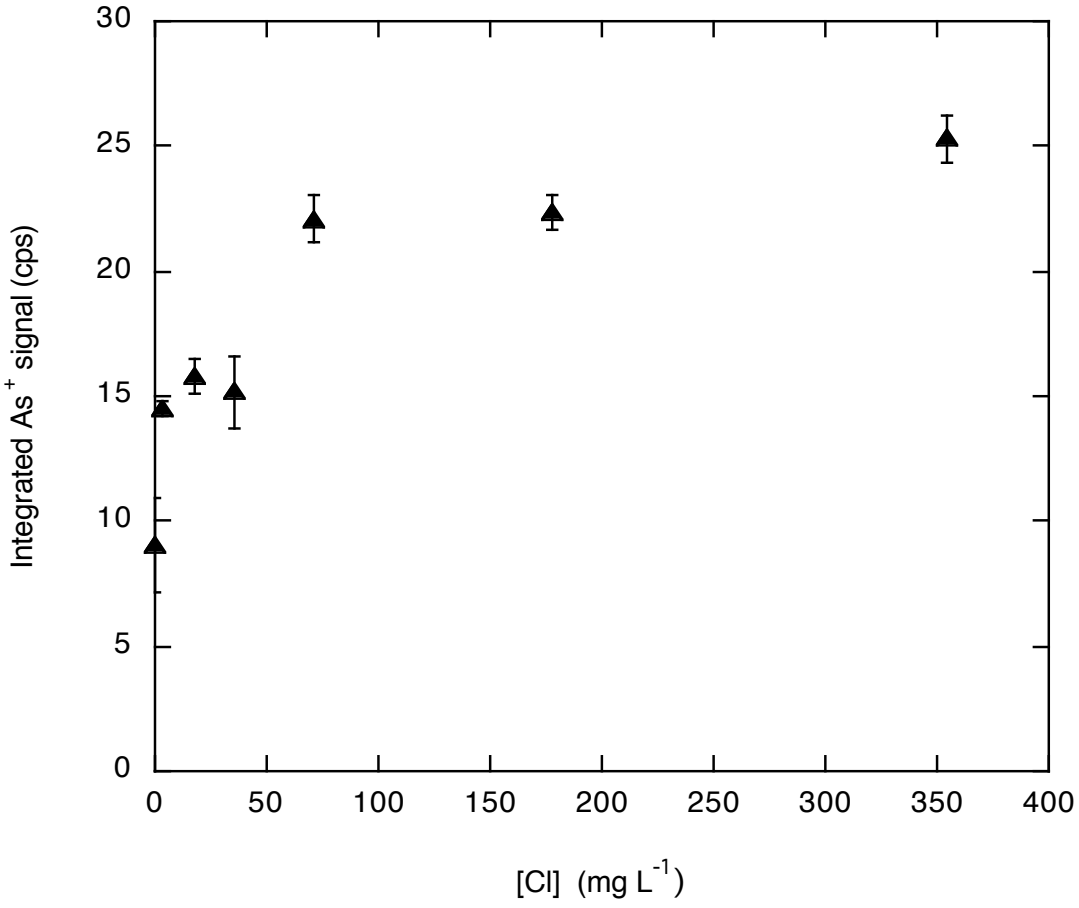

Figure 5.3. Effect of increasing [Cl] on As^+ signal. Standards were run in triplicate; error bars correspond to one standard deviation.

5.4.2 Drinking water samples

Standard addition curves for bottled water samples A–C and diluted tap water are shown with the corresponding lines of best fit in Figure 5.4. The *x*-intercepts of the regression lines were used to calculate the ambient As concentrations in each sample, which are listed in Table 5.3. Table 5.3 also includes the slopes of the regression lines and the approximate chloride concentration of each water sample, estimated by comparing the ratio of the sample $ArCl^+$ peak area to that of standards containing 35.5 mg Cl L^{-1}. The calibration curves for both the mountain spring waters and diluted tap water have approximately the same slope, whereas a smaller slope was observed for the bottled water treated by reverse osmosis. Since these slopes are all steeper than the slopes of the standard calibration curves for both 0 and 35.5 mg Cl L^{-1}, the presence of other ions in the matrix must affect the As signal.

The concentrations for both As and chloride in Table 5.3 span a range of As and Cl levels that would be expected for drinking water in the U.S. Tap water contained the highest [Cl]; the measured value falls between the average Cl concentrations for Pasadena well water (30 mg L^{-1}) and imported water (79 mg L^{-1}) (PWP, 2004). Both tap water and bottled water B, which came from a mountain spring of volcanic origin, contained greater than 1 μg L^{-1} As. Bottled water C, which consisted of tap water treated by reverse osmosis, had negligible Cl and As levels approaching the detection limit for this method.

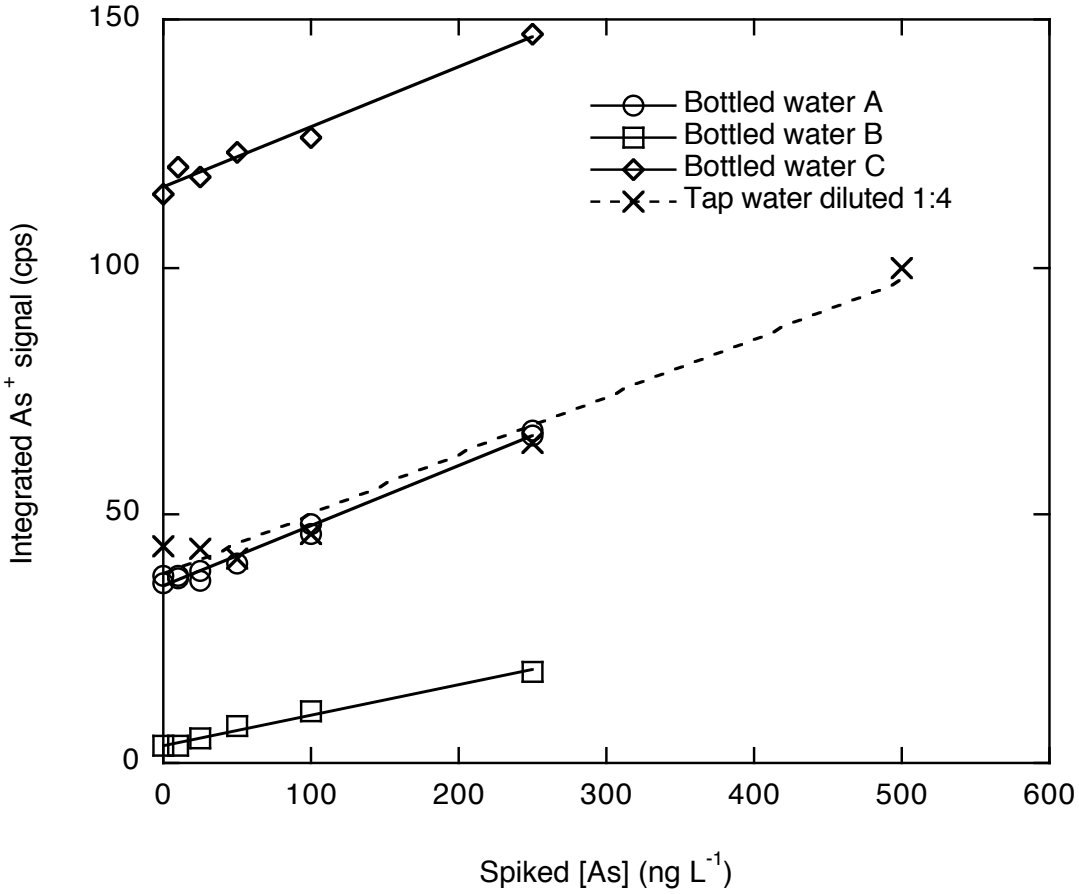

Figure 5.4. Standard As addition curves for bottled and tap waters.

Table 5.3. Characterization of water samples.

Sample	Slope	[As] (μg L^{-1})		Approximate [Cl][b] ($mg\ L^{-1}$)
		ambient	as measured[a]	
Bottled water A	0.121	0.330	0.290	Trace
Bottled water B	0.121	1.100	0.960	20
Bottled water C	0.0611	0.066	0.060	Trace
Tap water	0.119	1.300	0.320	50

a: as measured refers to values determined for diluted samples

b: Approximate [Cl] was calculated using the ratio of the sample $ArCl^+$ signal to that of the 35.5 mg Cl L^{-1} standards

5.5 Discussion

Using a commercially available high resolution ICP-MS instrument, As^+ and $ArCl^+$ peaks could be resolved, thus obtaining an MDL nearly 50 times lower than the average MDL for transmission quadrupole ICP-MS analysis and 8 times lower than that derived by Klaue and Blum (1999) using a high resolution ICP-MS instrument (R = 7800-9200). Moreover, this method has not been optimized. More rigorous method development, such as decreasing the mass scan windows to measure only the high count regions of the peaks, shielding the torch, or using a more effective nebulizer, would likely yield an even lower MDL in shorter sample run times. Although PQLs are always greater than the corresponding MDLs, typically the PQL for a given contaminant is no more than 3–10 times the MDL. Even taking the upper bound, this would yield a PQL value 10 times smaller than the current PQL for As.

Numerous studies have achieved very low detection limits for arsenic, some even in the presence of high Cl matrices such as seawater and urine. However, the challenge here is not developing the analytical instrumentation to detect very low concentrations of As, but rather developing the *widespread* ability to measure low As levels quickly and routinely in commercial or utility laboratories throughout the U.S., without elaborate or time-consuming sample processing. Since As is just one of many regulated contaminants, it is desirable that the method used for As be easily adaptable to other pollutants. Due to its high sensitivity and ability to quantify most inorganic contaminants (and some organics when coupled with chromatographic techniques), ICP-MS is an ideal technology for this application. High resolution ICP-MS and several modified low resolution ICP-MS methods are outlined with their corresponding As MDLs in Table 5.4.

Note that all matrices studied are either drinking water or prepared samples with elevated Cl concentrations; in the latter case, the reported MDL is likely an upper bound for the detection limit that would be obtained for drinking water.

High resolution ICP-MS allows $ArCl^+$ ions to reach the detector, but has the capability of distinguishing them from As^+ ions. In contrast, low resolution ICP-MS instruments equipped with collision/reaction cells, mixed-gas plasma, membrane desolvation, or electrothermal vaporization provide online methods of minimizing the $ArCl^+$ interference. In collision/reaction cell ICP-MS, ions enter a collision cell in which polyatomic interfering ions such as $ArCl^+$ are converted into noninterfering species via interactions with a reaction gas (e.g. H_2, He). In contrast, mixed-gas plasma ICP-MS is designed to suppress the initial formation of $ArCl^+$ ions by introducing a small fraction of N_2 or organic solvent with the sample. This has an additional benefit in that it can increase the sensitivity of elements with low ionization potentials, such as As (Beauchemin 2004). In membrane desolvation, the sample, after being aerosolized, enters the membrane desolvator where the more volatile matrix components (e.g. water, HCl, and in other applications, organic solvents) pass through a microporous membrane and are removed prior to ionization. Finally, in electrothermal vaporization ICP-MS, the nebulizer is replaced by a carbon furnace or metal filament, which dries, chars, and vaporizes the sample when heated. The temperatures of vaporization are controlled such that different analytes vaporize and enter the ICP-MS at different times, thus effectively allowing the component of interest to be thermally separated from the matrix.

Hydride generation and chromatographic separation are two well-established front end technologies that separate As from matrix Cl prior to ICP-MS analysis. In hydride