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Lowering the detection limit for arsenic: Implications for a future practical quantitation limit

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The practical quantitation limit (PQL) for arsenic (As) is currently orders of magnitude higher than its nonenforceable, health-based standard in California. Analytical limitations caused by chloride (Cl) interference can be overcome using high-resolution, inductively coupled plasma mass spectrometry (ICP/MS), which has a method detection limit for As of 29 ng/L in the presence of 35.5 mg/L Cl. Increasing Cl concentration (0–355 mg/L) resulted in a nonlinear increase in the As signal. Therefore, standard addition was used to test four water samples with unknown As and Cl concentrations. Because standard addition is not suitable for routine analyses, further investigation of matrix effects and interferences is needed to optimize the application of high-resolution ICP/MS for water quality testing. Nonetheless, broader adoption of this and other methods for trace As analysis could result in lowering of the PQL for As in the future, with consequent downward pressure on reporting levels.

Lowering the detection limit for arsenic:

Implications for a future practical quantitation limit

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Exposure to arsenic (As) in drinking water is associated with an increased risk of bladder, liver, kidney, and skin cancers (Smith et al, 2002; NRC, 2001). To mitigate these risks, the US Environmental Protection Agency (USEPA) revised the maximum contaminant level (MCL) for As in 2001. After considering possible standards ranging from 5 to 20 µg/L, USEPA set the MCL for As at 10 µg/L with a compliance date of January 2006 (USEPA, 2002). States have the option to set their own regulatory standards at or below the federal MCL; the New Jersey standard is 5 µg/L (NJDEP, 2004), and other states, such as California, are currently evaluating their state MCLs. These enforceable standards must be set as close to corresponding, nonenforceable health-based standards as is feasible and be justified by a cost–benefit analysis. The federal health standard, the MCL 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 based on an excess risk of 10^{-6} from lifetime water consumption of 2 L/d per person.

The major factors that determine whether an MCL value is feasible are the analytical capabilities and the cost of treatment. Because treatment costs can be difficult to estimate, analytical limitations sometimes serve as convenient criteria for feasibility. Regulatory enforcement requires that routine measurements of the tar-

get contaminant be reliable. Thus USEPA establishes practical quantitation limits (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 operating conditions. Because compliance monitoring must be supported by the analytical capabilities of a sufficient number of laboratories, the PQLs are used by USEPA to make decisions about analytical feasibility. Some 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 because of variations in instrument response or operator capabilities. Although the PQL is usually defined on the basis of an interlaboratory study, in the absence of such data, the PQL is typically set to five times the average MDL (Eaton, 1994).

For As, the PQL is nearly three orders of magnitude greater than California's PHG (Table 1). The national average MDL using transmission quadrupole ICP/MS is 1.4 µg/L (Creed, 1994). This value, although lower than the PQL, is still 350 times higher than the California PHG. The MDL for transmission quadrupole ICP/MS is limited by an interference derived from the presence of chloride (Cl) in the drinking water matrix. In the argon (Ar) plasma, an argon chloride (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 article 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 attention to the variety of methods that may allow the As PQL to be lowered in the future.

This issue of analytical constraints on the feasible level for the MCL is not limited to As. Numerous examples exist of drinking water contaminants for which the current PQL is higher than the MCLG or California's

PHG (Table 1). Although some reporting requirements and even state drinking water standards (e.g., for heptachlor) may fall below the PQL, it is also true that a given chemical contaminant may receive little attention if its concentration falls below the current PQL. This article seeks to point out that such practices ignore the rapid development of analytical capabilities, which could serve as a basis for future re-evaluations of the PQL. Reliance on the current PQL in defining a feasible MCL may leave enforceable standards open to future challenges. Although the PQL is only one contributing factor in revising an MCL, As 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.

METHODS AND MATERIALS

Calibration standards. All solutions were prepared in new polypropylene tubes that were acid-washed in 5% nitric acid.[1] Arsenic calibration standards[2] ranged from 2.5 to 2,500 ng/L and were prepared in 1% nitric acid.[1] Analytical-grade sodium chloride[3] was added to some standards to achieve Cl concentrations ranging from 3.55 to 355 mg/L. All solutions were prepared gravimetrically.

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 United States and abroad, respectively, and bottled water C was purified US tap water. Because of the unknown matrixes (in particular, Cl concentrations) for all four water sam-

TABLE 1 Regulated water contaminants with practical quantitation limits higher than corresponding health goals

| Contaminant	MCL µg/L	PQL µg/L	MCLG µg/L	CA MCL µg/L	PHG µg/L
Arsenic	10	3	0	50*	0.004
Cadmium	5	2	5	5	0.07
Thallium	2	2	0.50	2	0.10
Benzene	5	5	0	1†	0.15
Benzo(a)pyrene	0.20	0.20	0	0.20	0.004
Dichloromethane	5	5	0	5	4
Heptachlor	0.40	0.40	0	0.01†	0.008
Heptachlor epoxide	0.20	0.20	0	0.01†	0.006
Hexachlorobenzene	1	1	0	1	0.03
Pentachlorophenol	1	1	0	1	0.40
Vinyl chloride	2	2	0	0.50†	0.05

Sources: CADHS, 2006; USEPA, 2005, 2002a, 1999

CA MCL—California maximum contaminant level, MCL—maximum contaminant level, MCLG—maximum contaminant level goal, PHG—public health goal, PQL—practical quantitation limit

*The CA MCL is undergoing revision, but California is currently accountable for meeting the federal MCL.
†In these cases, the CA MCL is set lower than the PQL, forcing California utilities to achieve a lower detection limit to ensure they are meeting the standard.

FIGURE 1 Peak separation for As$^+$ and ArCl$^+$
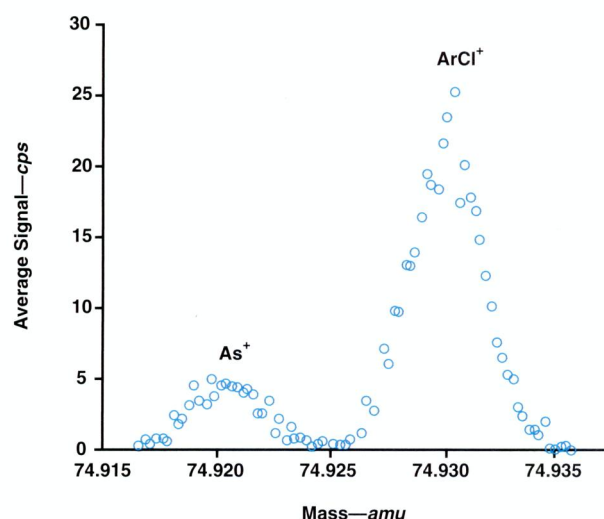
Conditions: [As] = 50 ng/L, [Cl] = 35.5 mg/L

TABLE 2 Inductively coupled plasma/mass spectrometry operating and data collection conditions

Condition	Value
Radio frequency power—W	1,297
Plasma cool gas—L/min	15.1
Auxiliary gas—L/min	1.0
Sample gas—L/min	0.97
Sample flow rate—$\mu L/min$	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

sponded to a measured resolution (R) of 7,900–10,000, in which

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

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. Because 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 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 so that the As$^+$ and ArCl$^+$ peaks remained centered.

RESULTS

Instrumental calibration and detection limits. An example of As$^+$ and ArCl$^+$ peak separation is shown in Figure 1. After quantifying such peaks, calibration curves were generated for standards with both 0 and 35.5 mg/L Cl (Figure 2). Because of 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 and [Cl] varied from 3.55 to 355 mg/L (Figure 3). The upper limit of this range is below the secondary MCL for Cl (500 mg/L) 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. For [Cl] less than 70 mg/L, the dependence on [Cl] is stronger, but there is less interference with the As$^+$ signal. In contrast, for [Cl] greater than 70 mg/L, the effect on the As$^+$ signal is greater but it no longer changes significantly with increases in [Cl]. The threefold increase in As$^+$ signal as [Cl] was varied from 0 to 355 mg/L and was not problematic in this study because samples with unknown Cl levels were analyzed using the method of standard additions.

The instrument detection limit, defined as three standard deviations above the mean blank signal ($n = 7$), was 13 ng/L. 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.

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

ples, 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 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.

Analytical method. Samples were run on a magnetic sector field ICP/MS instrument[4] using a microflow nebulizer[5] and a Peltier-cooled cyclonic spray chamber.[6] The instrument was set on high-resolution mode. Depending on instrument tuning conditions, this setting corre-

4. The x-intercepts of the regression lines were used to calculate the ambient As concentrations in each sample, which are listed in Table 3. Table 3 also includes the slopes of the regression lines and the approximate Cl concentration of each water sample, estimated by comparing the ratio of the sample ArCl$^+$ peak area to that of standards containing 35.5 mg/L Cl. 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. Because these slopes are all steeper than the slopes of the standard calibration curves for both 0 and 35.5 mg/L Cl, the presence of other ions in the matrix must affect the As signal.

The concentrations for both As and Cl in Table 3 span a range of As and Cl levels that would be expected for drinking water in the United States. Tap water contained the highest [Cl]; the measured value falls between the average Cl concentrations for Pasadena (Calif.) well water (30 mg/L) and imported water (79 mg/L; PWP, 2004). Both tap water and bottled water B, which came from a mountain spring of volcanic origin, contained greater than 1 µg/L 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.

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 & Blum (1999) using a high-resolution ICP/MS instrument (R = 7,800–9,200). 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 interlaboratory MDL. Taking the upper bound into account for higher possible detection limits resulting from analysis by other laboratories or from blind unknowns, this would yield a PQL value 10 times smaller than the current PQL for As.

A larger increase in As$^+$ counts was observed with increasing [As] for drinking water samples compared with standards containing only As and HNO$_3$ in the presence or absence of Cl. Elements that have higher first ionization potentials than As, such as carbon, selenium, and Cl, enhance the As signal on ICP/MS by allowing As atoms to be preferentially ionized in the plasma (Park et al, 2002). However, the effect of [Cl] on As$^+$ counts is primarily because of overlap between the As$^+$ and ArCl$^+$ peaks rather than differences in ionization potential, and,

on the basis of the relatively small change in slope resulting from 35 mg/L Cl addition, different ionization potentials of other matrix constituents are unlikely to account for the entire effect on the observed slopes. A second matrix effect that likely contributes to the difference in experimental slopes involves the difference in ionic strengths between the sample waters and the standards. Ionic strength can affect nebulized droplet formation (Kebarle & Peschke, 2000) and plasma ionization temperature (Roos et al, 2006), both of which can strongly

FIGURE 2 Standard As calibration curves

$y = 0.0554x + 1.60$

$y = 0.0308x + 1.41$
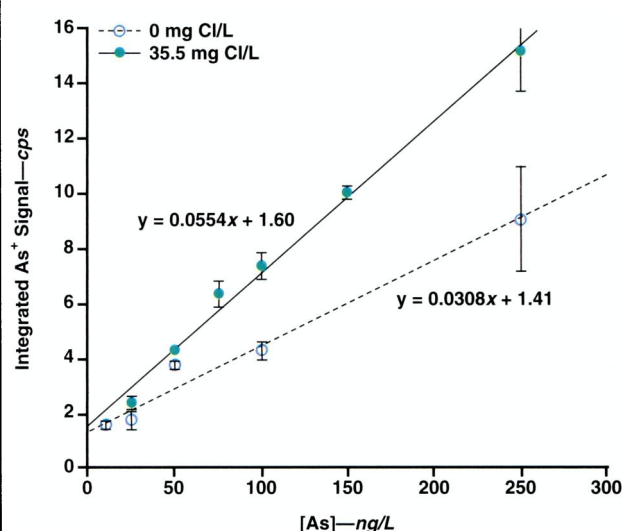
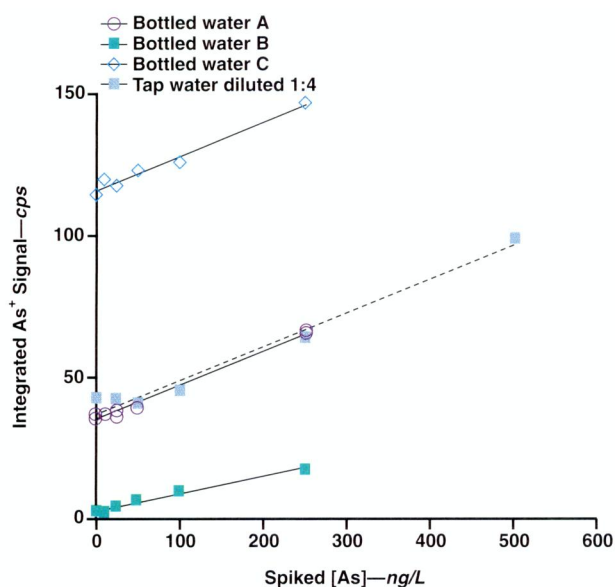*Standards were run in triplicate; error bars correspond to one standard deviation.*

FIGURE 3 Effect of increasing [Cl] on As$^+$ signal
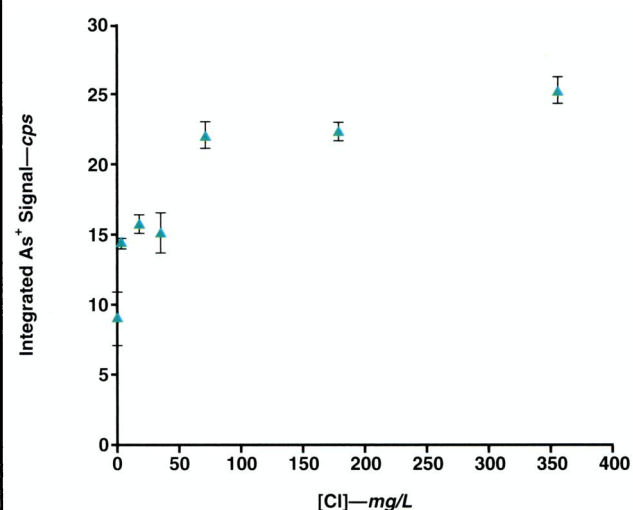
Standards were run in triplicate; error bars correspond to one standard deviation.

FIGURE 4 Standard As addition curves for bottled and tap waters

influence ion signals (Thomas, 2003). Addition of small fractions of solvents or surfactants such as ethanol, methanol, or sodium dodecylsulfate has been used to overcome these physical effects (Liu & Beauchemin, 2006; Hu et al, 2005). Although the changes in slope were not problematic for this study because the method of standard additions was used, the current approach would not be practical for routine water analysis. Further work on overcoming these matrix effects is needed before this method could be used routinely on a broad scale. For specific water sources that are not changing significantly over a given time period, standard additions could be used for the initial analysis, and subsequent samples could be tested using the generated calibration curve.

Numerous studies have achieved very low detection limits for As, some even in the presence of high Cl

matrixes such as seawater and urine. However, the challenge here is not to develop the analytical instrumentation to detect very low concentrations of As, but rather to develop the widespread ability to measure low As levels quickly and routinely in commercial or utility laboratories throughout the United States without elaborate or time-consuming sample processing. Because As is just one of many regulated contaminants, it is desirable that the method used for As be easily adaptable to other pollutants. Because of 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 4. Note that all matrixes 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., hydrogen, helium). In contrast, mixed-gas plasma ICP/MS is designed to suppress the initial formation of $ArCl^+$ ions by introducing a small fraction of nitrogen or organic solvent with the sample. This has an additional benefit of increasing 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, hydrochloric acid, and, in other applications, organic solvents) pass through a microporous membrane and are removed before 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, 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

TABLE 3 Characterization of water samples

| Sample | Slope | [As]—μg/L | | Approximate [Cl]† mg/L |
		Ambient	As measured*	
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

*"As measured" refers to values determined for diluted samples.
†Approximate [Cl] was calculated using the ratio of the sample $ArCl^+$ signal to that of the 35.5 mg/L Cl standards.

before ICP/MS analysis. In hydride generation ICP/MS, addition of sodium tetrahydridoborate reduces As to gaseous arsine hydride, which is subsequently introduced into ICP/MS (or atomic fluorescence spectroscopy), leaving the liquid matrix and associated Cl behind. Chromatographic techniques such as liquid chromatography or ion chromatography followed by ICP/MS analysis also separate As species from Cl and other matrix constituents before introduction of the sample into the mass spectrometer. Both hydride generation and chromatographic separation can be used to determine As speciation, which may be useful in some water quality applications.

Each ICP/MS technique discussed here can be hybridized with other methods. For example, As has been analyzed by combinations of liquid chromatography and collision cell ICP/MS as well as liquid chromatography and hydride generation ICP/MS, yielding MDLs of 22 and 4.2 ng/L in 2% Cl solution (Nakazato et al, 2002). In addition, the same ICP/MS instrument can be used with different accompanying methods to optimize performance for the analytes of interest. The variety of options for detection of As at trace levels suggests that the capability for such measurements could become widespread in response to future demand.

By definition, a PQL can only be based on routine analytical methods. In addition, methods that quantify multiple drinking water contaminants concurrently are clearly advantageous. Although hydride generation ICP/MS has an MDL lower than California's PHG for As, the method is element-specific and is therefore not likely to be the basis for a lower PQL for As. For the same reason, chromatographic techniques will probably not be widely used

by water quality laboratories. However, the other modified ICP/MS technologies are readily applicable to a large suite of analytes. High-resolution ICP/MS and collision cell ICP/MS show particular promise for widespread adoption. Although prices for high-resolution ICP/MS instruments are still prohibitive, the costs have been declining with the advent of second-generation instruments (Vanhaecke & Moens, 1999), making it likely that use of such instruments will continue to grow. Collision cell ICP/MS (although not yet included by USEPA as an analytical method) is less expensive than high-resolution ICP/MS and can be operated so that the elements whose analysis benefit from the collision cell are analyzed first, whereas other elements are quantified after flushing the reaction gas from the collision cell. Broader use of these two forms of ICP/MS could facilitate a future revision of the PQL for As.

CONCLUSIONS

With a variety of techniques that are readily applicable to drinking water, it is likely—if not inevitable—that the PQL for As will be lowered in the future, requiring drinking water providers to report lower As values. Although As is discussed as the principal example in this study, the same trend is likely to occur with other regulated drinking water contaminants. If justified by the health benefits and the treatment costs, a lower PQL leaves the MCL open for revision, which may eventually require utilities to modify their treatment methods. These eventualities should be considered when planning for future treatment plant upgrades, expansion, or design, even for contaminants with concentrations that fall below current PQL values.

TABLE 4   Modified ICP/MS methods capable of measuring trace levels of As in the presence of matrix chloride

Method	Strategy for Dealing With ArCl+	Matrix	Method Detection Limit—ng/L
High-resolution ICP/MS	Resolves the As peak from the ArCl+ peak	Drinking water	29
		Drinking water plus up to 1 g/L Cl	260
Collision/reaction cell ICP/MS	ArCl+ interacts with reaction gas to form noninterfering species.	5% HCl	153
Mixed-gas plasma ICP/MS	Suppresses formation of ArCl+	Drinking water plus up to 1 g/L Cl	<300
		99 mg/L Cl	240–480
Electrothermal vaporization ICP/MS	Thermally preseparates As from the matrix	37% HCl	40
Membrane desolvation ICP/MS	Removes HCl in addition to water vapor prior to ionization	Drinking water plus up to 1 g/L Cl	100
Hydride generation ICP/MS	Preseparates As from the matrix by forming, trapping, and analyzing arsine hydrides	2% Cl	1.4–4.2
		Drinking water plus up to 1 g/L Cl	0.25
LC-ICP/MS or IC-ICP/MS	Chromatographically separates As species from chloride before introduction into ICP/MS	Drinking water	400–800
		2%Cl	57–116

Sources: Day et al, 2002; Hill et al, 1992; Klaue & Blum, 1999; Nakazato et al, 2002; Niemela et al, 2003; Thomas, 2003; and this research.

HCl—Hydrochloric acid, ICP/MS—inductively coupled plasma/mass spectrometry, IC-ICP/MS—ion chromatography inductively coupled plasma/mass spectrometry, LC-ICP/MS—liquid chromatographic inductively coupled plasma/mass spectrometry

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FOOTNOTES

[1] Omnitrace nitric acid, EMD Chemicals, Cincinnati, Ohio
[2] PlasmaCal ICP standard, SCP Science, Champlain, N.Y.
[3] ULTREX Ultrapure reagent, J.T. Baker, Phillipsburg, N.J.
[4] ELEMENT, Thermo Finnigan, Waltham, Mass.
[5] PFA-20, Elemental Scientific Inc., Omaha, Neb.
[6] PC3 SSI, Elemental Scientific Inc., Omaha, Neb.

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