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Trace Analyses of Arsenic in Drinking Water by Inductively Coupled Plasma Mass Spectrometry: High Resolution versus Hydride Generation

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A magnetic sector inductively coupled plasma mass spectrometer (ICPMS) was applied to the determination of arsenic in drinking water samples using standard liquid sample introduction in the high-resolution mode ($M/\Delta M$ = 7800) and hydride generation in the low-resolution mode ($M/\Delta M$ = 300). Although high mass resolution ICPMS allowed the spectral separation of the argon chloride interference, the accompanying reduction in sensitivity at high resolution compromised detection and determination limits to 0.3 and 0.7 μg/L, respectively. Therefore, a hydride generation sample introduction method, utilizing a new membrane gas−liquid separator design, was developed to overcome the chloride interference. Due to the high transport efficiency and the 50−100 times higher sensitivity at $M/\Delta M$ = 300, the HG-ICPMS method resulted in an over 2000-fold increase in relative sensitivity. The routine detection and quantification limits were 0.3 and 0.5 ng/L, respectively. The results for both methods applied to the analysis of over 400 drinking water samples showed very good agreement at concentrations above 1 μg/L. For concentrations between 0.01 and 1 μg/L, only HG-ICPMS provided accurate quantitative results. Membrane desolvation, mixed-gas plasmas, and the addition of organic solvents for the reduction of the $ArCl^+$ interference were also investigated and evaluated for trace As determination.

The second generation of magnetic sector inductively coupled plasma mass spectrometers (ICPMS) has now been widely accepted due to their outstanding performance characteristics and increasingly affordable prices.[1] The principles of modern magnetic sector ICPMS as well as the most prominent spectroscopic interferences have been described in the literature.[1−3]

The well-known polyatomic interference $^{40}Ar^{35}Cl^+$ at mass 74.930 69 amu hampers the analysis of the monoisotopic ^{75}As isotope ($^{75}As^+$ = 74.921 05 amu) even at moderate chlorine concentrations in the mg/L range and requires an $M/\Delta M$ of >8000 in order to achieve a full baseline separation of the peaks. Although the overall sensitivity of magnetic sector ICPMS instruments in the low-resolution mode of $M/\Delta M$ = 300 is at least 10 times higher than that for quadrupole instruments (and can further be improved by sample desolvation and the introduction of capacitive decoupling or ShieldTorch devices[4−7]), the sensitivity at $M/\Delta M$ = 7800 yields an intensity of only 0.5−2% compared to $M/\Delta M$ = 300.[1,8] In addition, due to its a high first ionization energy, arsenic shows a theoretical ionization efficiency of only 52%.[9] Therefore, peak top intensities for As in the high-resolution mode typically reach only a few hundred counts per second for 1 μg/L As with standard sample introduction systems.[8,10]

However, our drinking water study[11] required precise quantitative results for As even at sub-μg/L levels. After the first data set of 400 samples (including more than 40 blind duplicate samples) were analyzed and evaluated, it became evident that this was not achieved.

For accurate low-resolution ($M/\Delta M \leq 300$) ICPMS analyses of As in the sub-μg/L range, it is essential to either eliminate or correct for the ArCl interference. High-resolution ICPMS is an extremely useful tool for method development and testing because in some cases it is the only way to unequivocally distinguish between interference and true analyte, i.e., the blank signal. In the case of the ArCl interference, it can only be distinguished from the As blank itself in the low-resolution mode by measuring $^{40}Ar^{37}Cl$ and further isobaric Se isotope interference corrections.[10] Therefore, it is difficult to obtain precise low-level As analyses in matrixes with variable chlorine and selenium levels.

Due to the great number of samples (>2000) in our ongoing study of As in drinking water, it was also clear that time-consuming sample preparation techniques such as on- or off-line matrix separation methods[12−14] were not suitable. Recently developed instrumental methods, such as the removal of argon polyatomic

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species by ICP quadrupole ion trap mass analyzer systems,[15,16] were not available. Electrothermal vaporization is another possibility[17] but was neither available nor considered to be a practical solution. Therefore, four other approaches were evaluated: (a) introduction of N_2 to form a mixed-gas plasma;[18−20] (b) addition of organic solvents;[21] (c) membrane desolvation;[4,22] and (d) hydride generation.

Preliminary results as well as data from the literature[4,25] indicated that only membrane desolvation and hydride generation were valuable alternatives which could provide the required analytical performance. Due to the low cost, availability, ease of operation, and potential for additional applications,[23] the focus of our attention was to develop a hydride generation ICPMS method.

Since its introduction,[24] and particularly after the introduction of borohydride or tetrahydridoborate[25,26] as the reducing reagent, hydride generation (HG) has been coupled to many types of atomic spectrometry detection systems, including ICPMS.[27−31] Hydride generation has been used as an interface for the coupling of HPLC methods with ICP's for species analysis of arsenic compounds,[32,33] and recent developments in the on-line conversion of nonreducible arsenic species further improved its applicability.[34−36]

Selective chemical vaporization methods offer several important advantages over direct sample introduction because they provide a nearly 100% transport efficiency of the analyte while not loading the plasma with the matrix components. Nevertheless, chemical interferences and competitive reactions affect the reduction reaction in the samples and, hence, the efficiency or response of the HG reaction. The addition of L-cysteine as a reducing agent has been proven to practically eliminate matrix effects from d-group elements.[37,38] Also, HG can only reduce certain As species while others are not reducible at all. Additionally, all of the reducible As species show different responses. This has important implications for the sample preparation for HG analyses.[39,40] For our application of drinking water analysis, it was necessary to convert all inorganic arsenic to either As(III) or As(V). Most authors prefer to reduce inorganic As to As(III) with a variety of reagents, potassium iodide being the most widely used.[37] This is mostly because of the greater sensitivity of As(III) particularly for continuous-flow HG applications. The difference in sensitivity for As(III) and As(V) can be used to perform very fast and simple oxidation-state speciation analyses.[41,42]

Hydride generation can be applied in a continuous-flow reaction or in a batch mode. The continuous-flow mode applied in our study offers the substantial benefit of simple automation because it requires only the normal autoanalysis and nontransient signal evaluation routines of the ICPMS instrument.

The key component of HG is the gas−liquid separator (GLS), which separates the gaseous phase (hydrogen and arsine) from the liquid matrix when the reduction reaction is completed. The design of the GLS should provide optimal separation of the aerosol droplets created by the bubbling action of the evolving hydrogen gas and dampening of the comparatively noisy signal of the HG reaction. Most commonly used are U-shaped glass GLS designs, which typically provide high reaction efficiencies[46] and small dead volumes[47] but tend to show higher signal RSD's and are less efficient in separating fine aerosol droplets. This is also true in cases where a regular spray chamber was used as a GLS.[48,49] To obtain the complete gas−aerosol separation, membrane GLS's have become very popular.[43−45] The liquid phase is kept within a porous PTFE membrane or microporous PTFE tubing, and only the evolving gases are flushed into the plasma by an external Ar sweep gas flow. This kind of GLS has certain limitations regarding the optimization of the HG chemistry. In addition, the membranes age over time and are prone to clogging.[44,46]

We developed and used for this study a new type of membrane GLS which is based on a very robust design and offers practically complete gas−liquid separation, high signal stability, and a very low dead volume. In this paper, we report our investigation of As determinations in drinking water samples by high mass resolution and hydride generation ICPMS. Membrane desolvation and mixed-gas ICPMS techniques were also tested for their applicability in the presence of expected levels of chlorine. High-resolution ICPMS and (low-resolution) hydride generation ICPMS analyses

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were performed on the same subset of 400 individual drinking water samples for total As concentrations. HG analyses were performed on a total of 1000 individual samples, including 110 blind duplicate samples which were included for internal quality assurance purposes.

EXPERIMENTAL SECTION

Instrumentation. (a) ICPMS. All measurements were performed on a Finnigan MAT ELEMENT magnetic sector ICPMS. The instrument has three different mass resolution settings (R = 300, 3000, 7500 $M/\Delta M$) which are often referred to as "low", "medium", and "high" resolutions. The true or observed resolution depends on the particular instrument, ion optic system optimization, and slits and is typically higher than the minimum specifications mentioned above. In this case, the observed $M/\Delta M$ values were 400, 3800, and 7800−9200 for the three settings.

(b) High-Resolution ICPMS Measurements. The standard liquid sample introduction system consisted of a micro concentric nebulizer (MCN-2, CETAC Technologies) coupled to the standard Finnigan Scott-type double-pass spray chamber which was cooled to 1 °C. For sample transport, an eight-roller peristaltic pump was used with 0.19 mm i.d. Tygon tubing (Norton Performance Plastics). PEEK microtubing (0.125 mm i.d., CETAC) was used for the connections to the ASX-100 autosampler (CETAC) and to the MCN. Flow rates were adjusted to 0.08 mL/min. Instrument settings were optimized for sensitivity as well as for resolution with a solution containing 0.1 mg/L As and 500 mg/L Cl. For the As and ArCl signal, it was found that, in general, ArCl could be reduced by up to 50% at slightly higher sample gas flow rates by sacrificing less than 10% of the As intensity. Mass calibration and mass stability are very critical parameters for high-resolution ICPMS measurements, and mass calibrations were necessary several times a day. Yttrium was used as an internal drift control standard at a concentration of 10 μg/L. The general instrumental operating conditions are summarized in Table 1.

(c) Membrane Desolvation. The membrane desolvation unit used was an MCN6000 (CETAC) equipped with the same MCN-2 nebulizer. About 1% N_2 gas was added to the sample gas stream to further enhance the signal. Operating conditions were not varied from the conditions suggested by the manufacturer. The effectiveness of the ArCl suppression was investigated at $M/\Delta M$ = 7800 (Table 1).

(d) Mixed-Gas Plasma. Nitrogen additions of 0.5−5% of the 1.3 L/min total sample gas flow were achieved with a second mass flow controller and a 10% N_2 in Ar mixture. Methanol, ethanol, and isopropyl alcohol were added in concentrations of up to 20% to the sample solutions. The setup and operating conditions were the same as those for the other high-resolution ICPMS measurements (Table 1).

(e) Hydride Generation. We designed a new membrane GLS as shown in Figure 1. This design combines the effectiveness of a standard U-shaped GLS with the lower signal noise and better aerosol separation capabilities of a tubular membrane GLS. The membrane or filter is not in direct contact with the liquid and, therefore, has no tendency to clog or age over time. The total dead volume of the unit amounts to only 35−40 mL. The sample solution, acid solution, and borohydride/NaOH mixture are combined in a four-way PTFE cross connector and pass through a 10 cm long, 1.6 mm i.d. FEP reaction tube into the borosilicate glass GLS. The tip of the reaction tube touches the glass wall of the GLS to obtain maximum contact of the argon stream with the liquid phase. The reaction chamber is flushed with the "sample" gas flow. The porous membrane consists of a fine PTFE fiber filter (Zitex, Norton Performance Plastics) which is held in place by a KIMAX joint with a Viton O-ring seal. The second "spare" gas flow enters above the top of the membrane. The gas mixture is then fed into the ICP torch by a 25 cm long, 1.6 mm i.d. piece of FEP tubing. The tubing is tapered at the end and pressed firmly against the conical end of the sample gas tube of the torch to minimize the dead volume. The sample and reagent solutions and the drain are pumped by a four-channel peristaltic pump. For the sample and reagent flows, we used 0.76 mm i.d. and for the drain 2.79 mm i.d. Tygon pump tubing. For the drinking water analyses, no internal standard was used. Therefore, drift control was performed by reanalyzing an internal quality control standard after every 5−10 samples depending on the daily stability of the instrument and HG setup. Analysis data were only accepted if the drift between control standards was less than 3%. Additionally, 10% of the same samples were analyzed twice and results were

Table 1. Operating Parameters for High-Resolution (HR) ($M/\Delta M$ = 7800) and Hydride Generation (HG) ICPMS Measurements

	HR	HG
(a) Instrument Settings		
rf power (W)	1600	1300
plasma gas (L/min)	14.0	14.0
auxiliary gas (L/min)	1.0	1.0
sample gas (L/min)	1.3	0.3
spare gas (L/min)		0.7
sample flow rate (mL/min)	0.08	0.8
1 M HNO_3 flow rate (mL/min)		0.8
1% $NaBH_4$ flow rate (mL/min)		0.8
skimmer and sampler	Ni, 1 mm i.d.	
(b) Scanning Parameters		
resolution setting	7500	300
scan range As (amu)	74.912−74.932	74.897−74.947
scan range Y (amu)	88.897−88.915	
scan type	electrostatic	electrostatic
data points for 100% peak width	25	30
dwell time (s)	0.5	0.5
scan duration (s)	44	3
replicates	3	5
(c) Evaluation Parameters (%)		
peak search window	50	100
peak integration window	80	20

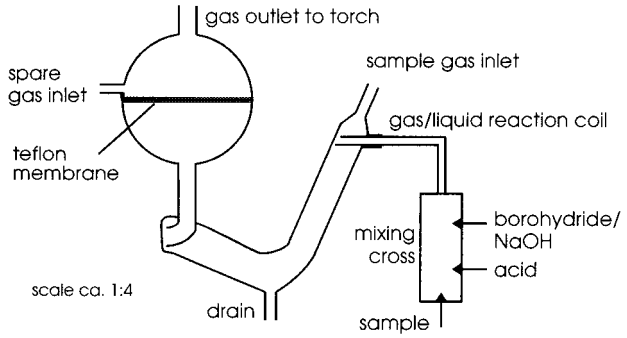

Figure 1. Schematic diagram of the membrane gas−liquid separator.

only accepted when they were within ±3% deviation. Blind duplicate samples (10% of the total samples) were also included in the sample set. HG analyses were performed in the low-resolution mode except for experiments to prove the ArCl reduction capabilities. The general operating parameters are listed in Table 1.

Reagents and Standard Solutions. All standard and reagent solutions were prepared with sub-boiled 18 MΩ deionized water. For sample acidification and the HG acid reagent ultratrace 65−70% nitric acid was used (Seastar). The sodium tetrahydridoborate GR and the Suprapur sodium hydroxide as well as the Suprapur hydrogen peroxide were purchased from Merck. Standard solutions were purchased from VHG Labs and High Purity Standards. Methanol, ethanol, and isopropyl alcohol (HPLC grade) were obtained from Fisher Scientific. Chloride matrix standards were prepared from ultratrace concentrated HCl (Seastar) and Suprapur NaOH. The 1% (w/v) sodium tetrahydridoborate solution was prepared by 10-fold dilution of a 10% stock solution in 1 M NaOH. The stock solution was kept refrigerated and remained stable for several weeks. HG standards were spiked to 0.1% hydrogen peroxide to oxidize all As to As(V).

Sample Collection and Preparation. The sample collection procedure has been described in detail elsewhere.[11] Sampling was carried out in acid-washed Nalgene (Nalge Nunc, Rochester, NY) 60 and 125 mL LDPE bottles and in commercially washed (I-CHEM) 125 mL HDPE Nalgene bottles. The samples were acidified to pH 1 with ultratrace nitric acid, and 0.1% hydrogen peroxide was added at least 24 h prior to analysis to oxidize all As(III) to As(V).

Reference Material. NIST (Gaithersburg, MD) SRM 1643d "Trace Elements in Water" was used for external quality control. The standard was used in undiluted form in 10-fold and 100-fold dilutions.

RESULTS AND DISCUSSION

High-Resolution Measurements. In the high-resolution mode, we typically obtained peak top sensitivities of 100−200 counts/s for 1 μg/L As for a new slit at a resolution of $M/\Delta M$ = 7800−8200. The resolution changed over the lifetime of the slit and actually increased over time while the transmission efficiency decayed. The change in resolution was caused by material that was sputtered off the low-resolution slit and deposited in the approximately 5−7 μm wide high-resolution slit. Therefore, at the end of the average high-resolution slit lifetime of about 300−400 operating hours, resolution changed from 7800 to 9800 but the sensitivity decreased by a factor of 4 to 50 counts/s for 1 μg/L As before the slits were replaced.

The mass calibration stability needs to be better than ±25% of the peak width (or 0.002 amu) to eliminate any impact of the ArCl interference on the evaluation of the As peak. Mass recalibrations were routinely performed after every 15 samples (about 60 min of analysis time).

The detection limit (DL) of 0.26 μg/L and quantification limit (QL) of 0.64 μg/L based on the calibration function (eight standard solutions ranging from 0.1 to 50 mg/L, correlation coefficient R^2 = 0.999 99, P = 95%) were largely controlled by the low count rates in the sub-μg/L range. Typically, As blank count rates were found to be in the range of only 3−8 counts/s. The detection limit (3σ) and quantification limit (10σ) method gave a theoretical DL of only 0.1 μg/L and a QL of 0.45 μg/L, respectively, but we believe this is overly optimistic for such low count rates. Therefore, only detection and quantification limits based on the actual calibration curve should be applied.[50] Nevertheless, the accuracy of the duplicate sample analysis for samples above 1 μg of As/L was typically in the range of 5−10% (Table 2). The overall correlation of the high-resolution ICPMS duplicate samples above the quantification limit shows a correlation coefficient R^2 = 0.996. For simple replicate analysis of the same sample within a batch, the precision was always better than ±5% for concentrations above 1 μg/L. The recovery rates for different dilutions of the NIST SRM 1643d are summarized in Table 3.

Table 2. Duplicate Drinking Water Sample As Analysis Results for High-Resolution (HR) ($M/\Delta M$ = 7800) and Hydride Generation (HG) ICPMS Measurements (μg/L)[a]

sample pair	HG		HR	
027/009	0.02	0.02	n.d.	n.d.
387/306	0.07	0.06	<0.64	<0.64
389/211	0.05	0.06	n.d.	n.d.
471/457	0.07	0.07	<0.64	n.d.
440/409	0.09	0.08	n.d.	<0.64
176/174	0.09	0.09	<0.64	<0.64
153/121	0.26	0.27	n.d.	n.d.
165/138	0.41	0.31	n.d.	<0.64
332/266	0.36	0.31	n.d.	<0.64
580/579	0.36	0.35	<0.64	<0.64
424/349	0.34	0.37	<0.64	<0.64
408/365	0.54	0.41	<0.64	0.66
123/087	0.59	0.55	<0.64	0.82
351/309	0.56	0.58	<0.64	<0.64
147/093	0.73	0.76	0.73	0.70
346/342	0.84	0.83	0.73	<0.64
399/343	0.70	0.86	<0.64	<0.64
555/449	2.55	2.53	2.44	2.43
180/036	9.47	10.2	9.25	9.45
368/268	34.3	33.3	34.1	34.7
543/438	48.9	49.2	47.1	50.0

[a] n.d., not detected/below 0.26 μg/L. <0.64, detected but below quantification limit.

Table 3. External Quality Control with NIST SRM 1643d for Hydride Generation (HG) and High-Resolution (HR) ($M/\Delta M$ = 7800) ICPMS Measurements (μg/L)

	certified	HG	HR
1643d	56.02 (±0.72)	57.5 (±2.1)	56.6 (±2.0)
1643d, 1/10	5.60 (±0.07)	5.53 (±0.18)	5.80 (±0.23)
1643d, 1/100	0.56 (±0.01)	0.57 (±0.02)	<0.64

The data set for the first 400 drinking water samples revealed that only 10% of the household waters showed As concentrations higher than 1 μg/L, 80% of the water samples were below the quantification limit of 0.64 μg/L, and more than 50% were below the DL of 0.26 μg/L. For the purpose of the drinking water study,[11] this meant that 80% of the samples were basically indistinguishable and, therefore, the quantification of very low levels of drinking water arsenic exposure was impaired.

The high-resolution ICPMS measurements at $M/\Delta M$ = 7800 also demonstrated that the ArCl interference, even in drinking

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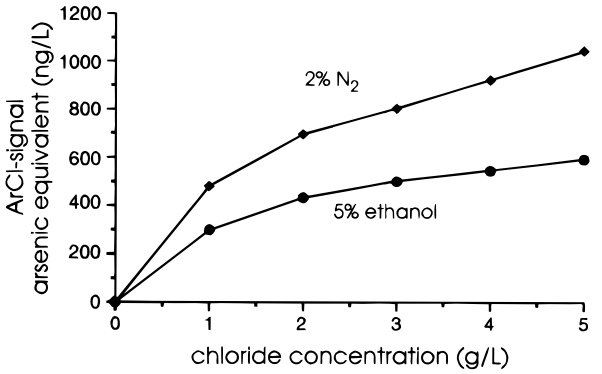

Figure 2. ArCl interference in equivalent As concentrations with standard sample introduction high-resolution ICPMS ($M/\Delta M = 7800$) for the addition of 2% N_2 to the sample gas flow and 5% (w/v) ethanol to the sample solution for different chloride concentrations.

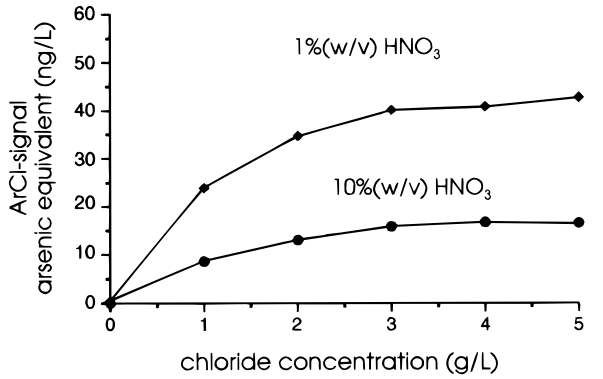

Figure 3. ArCl interference in equivalent As concentrations with membrane desolvation high-resolution ICPMS ($M/\Delta M = 7800$) for the addition of 1% and 10% HNO_3 to the sample solution for different chloride concentrations.

water samples with chloride levels typically below 1 g/L, are on average in the range of 0.5 μg/L equivalent As levels. The most extreme sample showed an equivalent As level of 4 μg/L or 400 counts/s peak top intensity for the ArCl signal.

Mixed-Gas Plasma Measurements. The introduction of nitrogen into the sample and cool gas flow can be used to suppress the formation of ArCl. Nitrogen levels of 0.5−5% in the sample gas stream were investigated in the high-resolution mode at different rf power levels and total sample gas flow rates. The sampling depth was not changed because of instrumental limitations of the ELEMENT torch box design. Nitrogen additions of more than 2% caused an intensity loss of the As signal without further improving the As/ArCl ratio. The best As/ArCl ratios were found at high rf power levels and slightly higher sample gas flow rates than those required for optimizing only the As signal intensity. The addition of 2% nitrogen yielded the best results and reduced the ArCl signal by a factor of about 5 while cutting the As equivalent concentrations from about 2−3 μg/L for 1 g of Cl /L to about 0.5 μg/L (Figure 2). This means that in a varying chloride matrix the low-level As results could be expected to show a bias of typically 0.1 μg/L, and in extreme samples up to 0.5 μg/L, due to the ArCl interference if no further elemental equation corrections were applied.

Alcohol additions to the sample solution itself have been reported to also effectively reduce chlorine interferences for As analyses.[21] We investigated the addition of methanol, ethanol, and isopropyl alcohol under the same conditions as for the addition of N_2. Alcohol was added to the samples at concentrations of 1, 5, 10, and 20%. It was found that the differences for the reduction of the ArCl interference for all three alcohols were basically negligible, but ethanol gave the highest increase in signal sensitivity (ca. a factor of 2) for As.[20,53] At concentrations above 5% ethanol, no further reduction of ArCl relative to the As signal was observed although the total sensitivities were still increased at higher alcohol concentrations. The results for the ArCl reduction of a 5% ethanol solution are also shown in Figure 2. The use of ethanol resulted in a slightly better ArCl reduction than for the nitrogen addition, but As equivalent concentrations of 0.3 μg/L for a 1 g/L chlorine matrix were still observed.

Both methods of creating mixed-gas plasma were capable of detection limits in the sub-μg/L range, but the accuracy in the presence of varying chlorine matrixes was inadequate.

Membrane Desolvation. Because of the high vapor pressure of HCl, membrane desolvation is capable of removing HCl together with the water vapor. Due to the higher diffusion coefficient of HCl compared to H_2O, the removal of HCl is less efficient.[51] To test the efficiency of the MCN6000 for HCl reduction, experiments were carried out to measure its water removal capabilities gravimetrically under standard operating conditions. For a sample uptake rate of 0.08 mL/min and a total sample gas flow of 1 L/min, the resulting water content was 0.15 mg/L, which equals ~1% relative humidity at room temperature.

Given the diffusion coefficient of HCl, the removal efficiency should therefore still be in the range of 99% for chlorine. This is only true for all chlorine in a given sample if it is completely displaced into the gas phase in the presence of stronger acids such as HNO_3. The chlorine removal efficiency is demonstrated in Figure 3 for different sodium chloride and nitric acid concentrations. Even though the nitric acid in the 10% solution was 100 times more concentrated than the Cl, it was not enough to completely remove the ArCl interference. This could be due to the HCl vapor removal efficiency or the crystallization of some sodium chloride in the remaining dry aerosol particles because of the fast drying process of small aerosol droplets at the given temperature.[52] The fact that the ArCl levels reach a plateau at chloride concentrations above 2 g/L can be explained by the diffusion processes.[51] Nevertheless, the plateau (or at least nonlinear behavior) of the ArCl response is similar to that observed for mixed-gas plasmas and could also be affected by plasma processes.

Although the removal of the ArCl interference was about 10 times more efficient using the MCN6000, the precision for As analyses in the sub-μg/L range for the expected chlorine levels was limited to ±10−25 ng/L due to the possible range of the equivalent ArCl signal. The dry aerosol introduction caused an overall intensity enhancement because of the reduction of the kinetic energy spread in the plasma and, hence, the better energy focusing of the ion beam. For As, this effect led to a 5-fold intensity increase for As(V). This improved the DL to the 50−100 ng/L range at $M/\Delta M = 7800$ but still did not yield the intensity increase needed to improve the QL by at least an order of magnitude.

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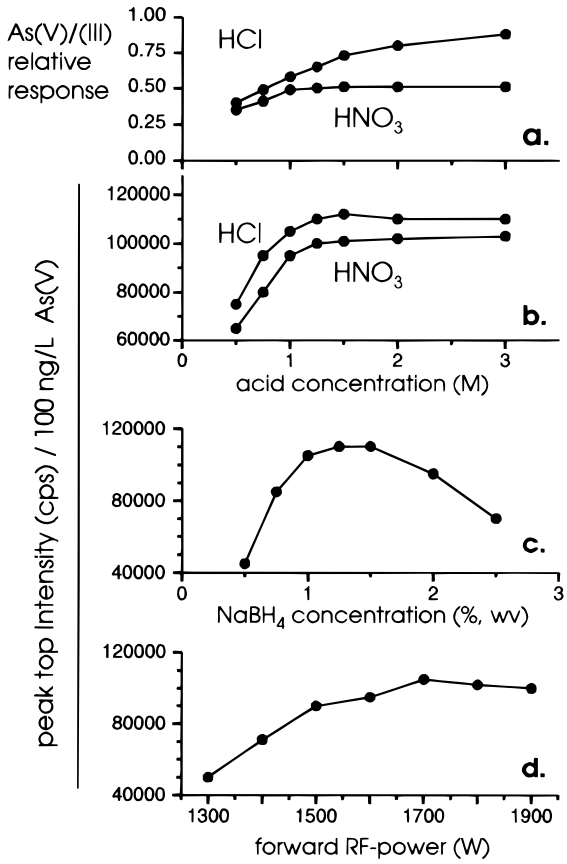

Figure 4. Optimization of the hydride generation ICPMS ($M/\Delta M$ = 300) system: (a) As(V)/As(III) response ratio and (b) As(V) intensity for different concentrations of HCl and HNO_3; (c) As(V) signal intensity as function of the $NaBH_4$ concentration and (d) As(V) signal intensity as a function of forward rf power.

The use of membrane desolvation also showed different responses for semivolatile species such as As(III) and As(V) as well as monomethyl and dimethyl arsenic acids. The recovery rate for As(V) compared to the Y signal was found to be 70% whereas the recovery rate for As(III) was only 40%. Another problem with the MCN6000 was discovered while we were investigating the washout behavior of the unit. We injected a 100 μg/L solution of As(V) for about 1 min, which represented the highest As concentration found in our water samples. Even after a rinse time of 25 min, the signal did not return to a stable background baseline, although we obtained stable signals for both blank measurements and As concentrations below 10 μg/L. For experiments with both mixed-gas plasmas and membrane desolvation, it is important to note that in all cases the actual As blank of the chloride interference check solutions always exceeded the intensity of the ArCl interference itself.

Hydride Generation. The optimization of the HG reaction regarding borohydride and acid concentrations as well as forward rf power is shown in Figure 4. Figure 4a demonstrates that only at very high HCl concentrations the relative response of As(V) and As(III) reached values of about 90%. We were not able to achieve equal responses for both species as reported by Creed et al.,[44] even when using concentrated HCl. The As(V)/As(III) relative response did not improve beyond 50% using nitric acid concentrations exceeding 1 mol/L. The sensitivity for HNO_3 was overall about 30% less than that for HCl (Figure 4b). The

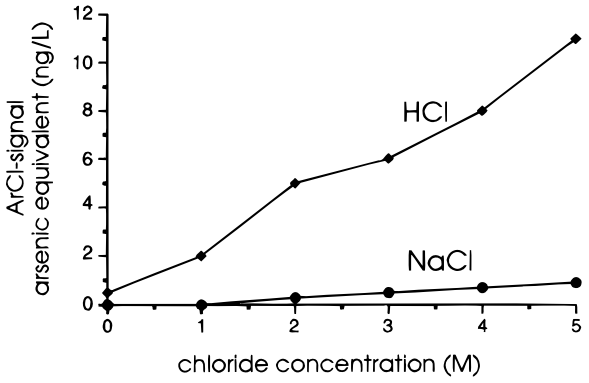

Figure 5. ArCl interference in equivalent As concentrations with hydride generation high-resolution ICPMS ($M/\Delta M$ = 7800) as a function of HCl and NaCl sample concentrations.

borohydride concentration optimized at 1−1.5% $NaBH_4$ in 0.1 M NaOH (Figure 4c). Due to the high cost of high-purity $NaBH_4$, 1% was chosen as the working concentration. The decrease of the As signal for higher $NaBH_4$ concentrations can be explained by the increased hydrogen gas load of the plasma. High rf power levels can be used to increase the signal level up to about 1700 W (Figure 4d), but for the low-resolution ICPMS HG analyses, we applied only 1300 W.

Figure 5 demonstrates, applying high-resolution HG measurements, why the use of HCl is less favorable for ultratrace As analysis with hydride generation ICPMS couplings unless an HCl vapor trap is employed. Using concentrated HCl solutions increased the HCl vapor load of the gas stream and, therefore, caused a significant contribution to the ArCl interference. The use of a similarly concentrated sodium chloride solution and 1 M nitric acid for the reaction solution proved that it was HCl vapor, and not remaining aerosol droplets, that caused the ArCl interference.

Due to the high sensitivity achieved even for As(V) (1000 counts/s peak top intensity for 1 ng of As /L at standard operating conditions (Table 1b)), it was not necessary to apply optimal conditions for the water analyses. In particular, the detection limits were strictly blank-determined due to the background concentration of As—mostly in the borohydride reagent. Therefore, we chose to oxidize all inorganic As in the sample solution by adding ~0.1% H_2O_2 24 h prior to the analyses. This treatment did not spoil the samples for other trace metal analyses and was performed together with the obligatory sample acidification.

Figure 6 demonstrates the effect and importance of the ratio of the two gas flows applied with our GLS design. Figure 6a shows how the ratio of the spare and sample gas flows changed the signal RSD (n = 10) for both the blank signal and a 10 ng/L standard solution. The lowest RSD was obtained when just the spare gas flow was used on top of the membrane because of the improved mixing of the arsine gas in the total gas flow. On the other hand, using just the sample gas flow through the reaction chamber transferred the signal noise of the irregularly bursting hydrogen/arsine gas bubbles. The absolute signal intensity was only marginally affected (Figure 6b). Therefore, the best detection limits could be achieved by using just the spare gas flow (Figure 6c). The tradeoff for not applying any sample gas flow was the dramatically increased washout times (Figure 6d), which were determined for a 100 μg of As/L sample introduction by the time

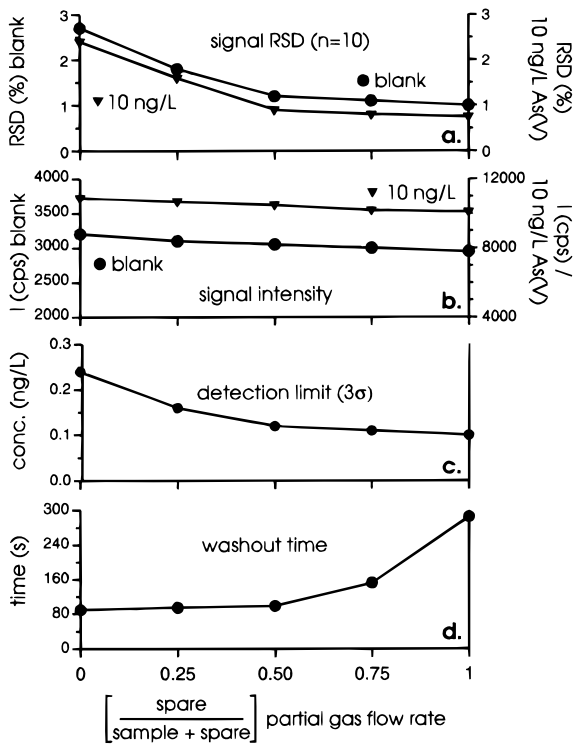

Figure 6. Optimization of the gas−liquid separator as a function of the spare and sample gas ratio: (a) signal RSD (n = 10) and (b) signal intensity for a blank and 10 ng/L As solution; (c) detection limit (3σ) and (d) washout time (at 0.01% level after 90 s of 100 μg/L As injection).

required to reduce the signal intensity below the 10 ng/L level. For these reasons, the best compromise operating conditions were found to be at a spare gas to sample + spare gas ratio in the range 0.5−0.7. Due to the low dead volume of the unit, steady-state signals were obtained after a 30 s injection into the GLS.

The relative detection and determination limits for the HG ICPMS, based on a calibration curve with seven standard solutions (ranging from 0.1 to 1 ng of As/L, R^2 = 0.994, P = 95%), were 0.25 and 0.53 ng/L. Even for continuous-flow injection with a signal stabilization time of 30 s, absolute detection limits of less than 50 fg were achieved. For practical reasons, the working range for the drinking water analyses (except field blanks) was limited from 10 to 10 000 ng/L using the analog counting mode of the ELEMENT detector system. On the basis of the linearity and homogeneity of variances, two linear working ranges from 10 to 1000 ng/L (R^2 = 0.99999) and from 1000 to 10 000 ng/L (R^2 = 0.99999) were applied, each calibrated with five to seven standard solutions. Standards were only accepted when they were within 3% deviation of the regression function.

Because only 5% of the samples in the entire data set showed As concentrations higher than 10 μg/L, those with higher levels were reanalyzed at 10-fold dilution. None of the samples were found to be below 10 ng/L. Field blanks showed concentrations of ~5 ng/L. The external precision of the HG method, determined by measuring the NIST 1643d standard, is given in Table 3.

Over 900 individual samples and 110 additional blind duplicate samples were analyzed by hydride generation ICPMS. The correlation coefficient for log−log transformed data of all duplicate samples was R^2 = 0.991. The concentration range below 100 ng/L yielded R^2 = 0.632 (N = 25) for the nontransformed concentration data, compared to 0.905 for the 0.1−1 μg/L range (N = 64) and 0.996 for duplicates above 1 μg/L (N = 21). The deviations for the low-level duplicate analyses represented true concentration differences rather than analytical errors because they were distinct samples. The precision for replicate analyses of the same sample was better than 5% even in the 10−100 ng/L range.

High Mass Resolution vs Hydride Generation ICPMS. Selected duplicate analysis results of both high-resolution and hydride generation ICPMS are compiled in Table 2 (21 duplicate pairs out of 44). For samples with concentrations below 1 μg/L, Table 2 displays deviations between duplicate samples that are sometimes above or below the DL of 0.26 μg/L. Samples that were detectable but below the QL are listed as <0.64 μg/L. For results below the quantification limit, it is evident that the precision for high-resolution ICPMS was poor or that the detection limit of 0.26 μg/L was not achieved. The correlation coefficient for all 400 samples analyzed with both high-resolution and hydride generation ICPMS was R^2 = 0.992 for the log−log transformed data above 1 μg/L. The excellent correlation of at least the quantifiable results with both independent methods indicates that neither method was hampered by severe matrix effects as would be expected for drinking water samples.

CONCLUSIONS

High-resolution ICPMS measurements of drinking water samples allowed the precise determination of As levels above 1 μg/L. The detection limit for routine analyses was found be in the range of 0.7 μg/L due to the relatively low sensitivity at $M/\Delta M$ = 7800. Applying the high-resolution mode of the ICPMS, other methods known to reduce the ArCl interference were investigated. Only membrane desolvation and hydride generation were successful in reducing the ArCl interference to an extent that made low-resolution ICPMS measurements in the sub-μg/L range possible. Hydride generation offered superior detection limits in the 0.2 ng/L range and complete ArCl removal even for high-chlorine matrixes. Additionally, HG can be used to greatly enhance detection limits for other reducible elements (Hg, Se, Sn, Sb, Te, Bi). High-resolution ICPMS measurements proved to be an important tool for investigating the effectiveness of ArCl removal and the optimization of As/ArCl response ratios. The magnetic sector instrument used in this study provided extremely high sensitivities for the HG method in the low-resolution mode.

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