Evaluation of iodine speciation and ^{129}I/^{127}I ratios at low concentrations in environmental samples using IC-ICP-MS

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Abstract

Subterranean radioiodine contamination at the Hanford Site in Washington State is believed to be present as iodide, iodate, and organo-I species, with iodate being the predominant form. Because these species have different sediment-sorption characteristics, understanding their distribution is important for developing an accurate understanding of iodine migration in the subsurface. Herein, we report a novel, rapid technique for simultaneous iodine speciation (iodide/iodate) and isotopic ratio (^{129}I/^{127}I) measurements using ion chromatography (IC) joined with collision/reaction cell inductively coupled plasma mass spectrometry (ICP-MS), collectively referred to as IC-ICP-MS. This approach employs online dynamically regenerated eluent suppression post chromatographic separation of the samples and collision cell technology, with pure oxygen as a collision gas for the active suppression of ^{129}Xe (which naturally exists in the argon supplied to the ICP source) to rapidly (< 15 min) achieve precise and reproducible results. Speciated standard reference materials yielded detection limits for ^{127}I of approximately 23.8 ng/L for iodate and 24.3 ng/L for iodide, and for ^{129}I of approximately 1.81 ng/L for iodate and 2.62 ng/L for iodide. The method was demonstrated by analyzing groundwater samples from six wells from ^{129}I-contaminated regions of the Hanford Site; iodate was the primary species for both ^{127}I and ^{129}I. Small quantities of ^{127}I-iodide were also detected in most of the samples, but all ^{129}I-iodide results were below the detection limit. An interference from molybdenum prevented the estimation of organo-iodine concentrations but did not affect the iodate and iodide results. This new analytical capability will enable rapid, simultaneous characterization of speciated inorganic iodine in vadose zone sediments and groundwater samples at levels below the US federal drinking water standard for ^{129}I of 1 pCi/L (~ 5.6 ng/L).

Keywords Radioiodine · Mass spectrometry · Iodine speciation · Iodine-129 · IC-ICP-MS · Ion chromatography

Introduction

Long-lived ^{129}I ($t_{1/2} = 15.7$ million years) is a highly mobile, radioactive isotope of iodine and a contaminant of interest in the vadose zone and groundwater at many nuclear facilities [1]. Radioiodine is a significant health risk due to the bioaccumulation factor of iodine in the thyroid gland, which can result in thyroid cancer, as has been epidemiologically confirmed after the Chernobyl accident [2, 3]. The Safe Drinking Water Act of 1974, mandated by the Environmental Protection Agency, established maximum contaminant levels for beta emitters, such as ^{129}I, which is currently regulated at 10 pCi/L (≈ 56 ng/L). The US Department of Energy (US DOE) set an even lower limit of 1 pCi/L (≈ 5.6 ng/L) based on a different dose conversion factor derived from the International Council on Radiation Protection Publication 30 [4], which is the lowest among all radionuclides in the Federal Register.

At the US DOE's Hanford Site in southeastern Washington State, large quantities of iodine isotopes, including ^{131}I and ^{129}I, were formed as a byproduct of nuclear fission in the site's nine reactors. The short-lived ^{131}I ($t_{1/2} = 8$ days) released from the fuel to the atmosphere in the 1940s is no longer a public health concern due to radiological decay over time [5]. However, the long-lived ^{129}I remains present in several large, dilute groundwater plumes resulting from production operation wastes that were discharged to the soil

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and subsurface [6]. These dilute ^{129}I groundwater plumes encompass an area of over 50 km^2 in the Hanford Central Plateau (Fig. 1). The highest groundwater concentrations (up to 22.8 pCi/L [≈ 128 ng/L]) have been measured in samples from the 200 West Area [6], while levels up to approximately 10 pCi/L (≈ 56 ng/L) have been observed in samples from the 200 East Area (Fig. 1) [7].

Radioiodine (^{129}I) fate and transport in both the vadose zone and groundwater is dependent on speciation due to differences in co-precipitation and sorption mechanisms for the various forms of iodine [8]. Therefore, identifying the species distribution is important for understanding subsurface radioiodine migration. At Hanford, the radioiodine is believed to be present as iodate (IO_3^-), iodide (I^-), and organo-iodine. Iodate is presumed to be the major species based on a limited characterization study [9]. In contrast, at the Savannah River Site in South Carolina, radioiodine is primarily in the form of iodide near the source term (F-Area Seepage Basins), but as the ^{129}I migrates away from the source, the distribution includes more iodate and organo-iodine [10–12]. Due to the biogeochemical differences of

each iodine species, speciation data can also be used to support the selection of optimal remediation strategies for iodine.

Presently, there exists no established analytical method for the rapid, direct determination of *speciated* ^{129}I/^{127}I analyses of natural samples at or below the federal drinking water standard. Due to an isobaric interference of ^{129}Xe (present in quantifiable amounts within the source argon (Ar) supply) on ^{129}I, inductively coupled plasma mass spectrometry (ICP-MS) is an analytical platform generally ill-equipped to analyze low-level perturbations of ^{129}I/^{127}I ratios. Because of this and the low levels at which ^{129}I must be quantified in groundwater, stable iodine (^{127}I) has been used as a proxy in past geochemical investigations of radioiodine fate and transport ([6, 8]; and references therein). However, because ^{127}I and ^{129}I have different sources, and their complex biogeochemical environments may not be in thermodynamic equilibrium, the species distributions may differ for the two isotopes. Therefore, independent ^{127}I and ^{129}I speciation measurements are required for the most accurate understanding of iodine speciation. When equipped with
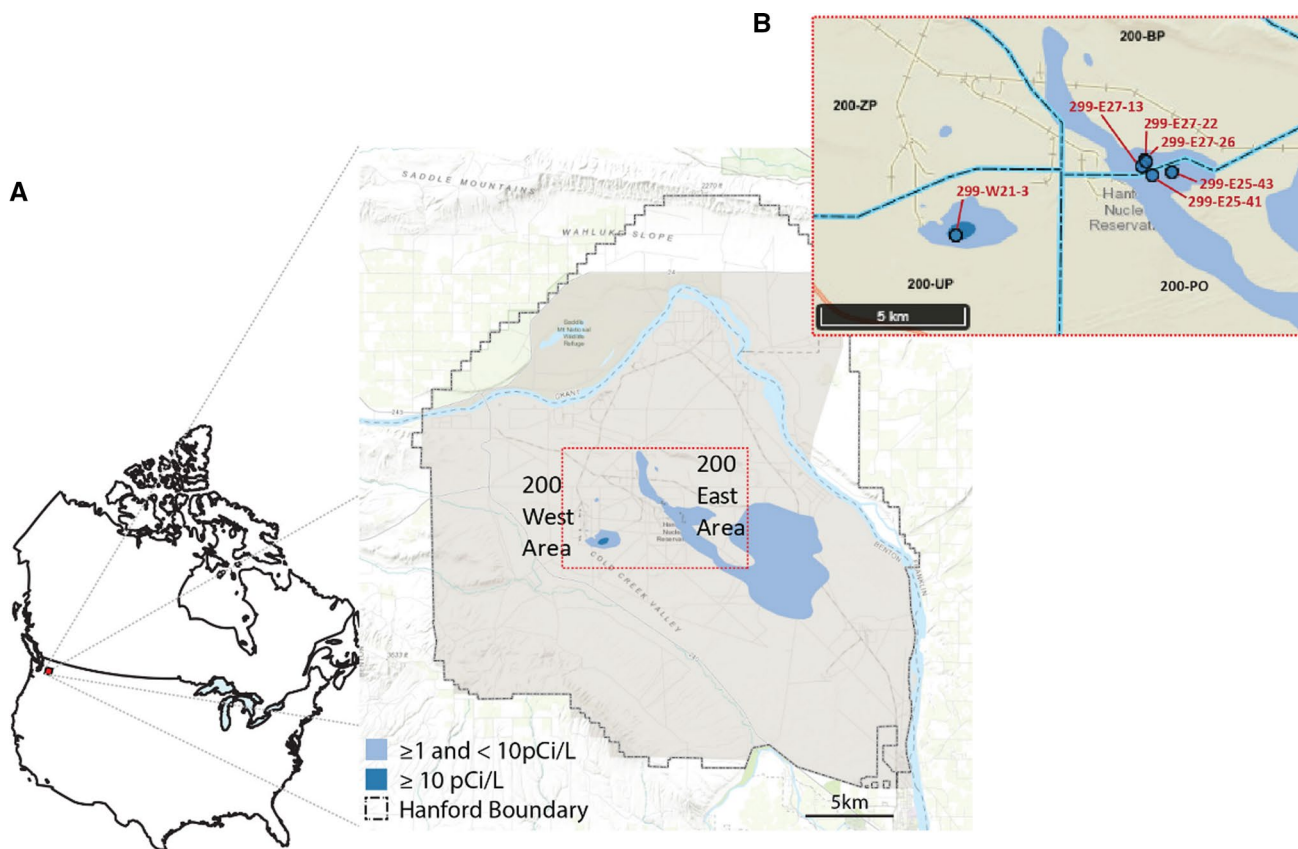

Fig. 1 **a** Map of ^{129}I groundwater contamination at the Hanford Site, located along the Columbia River near Richland, WA. The red dashed box denotes the sampling area for this study, as detailed in (**b**). **b** Well locations for groundwater iodine speciation measurements sampled in 2019–2020 by CH2M Hill Plateau Remediation Company for this study. Light blue shading denotes activity in solution between 1 and 10 pCi/L (5.6 ng/L and 56 ng/L). Dark blue denotes activity levels > 10pCi/L (> 56 ng/L). (Color figure online)

collision cell technology, ICP-MS has excellent potential to suppress isobaric interferences to manageable levels in order to discern deviations of $^{129}I/^{127}I$ in natural samples.

In this paper, we present a new, simple method using ion chromatography (IC) coupled to collision cell ICP-MS (IC-ICP-MS) that enables the rapid and simultaneous species separation and quantification of $^{129}I/^{127}I$ ratios in iodate and iodide in environmental samples at levels *below* the ^{129}I drinking water standard. Other researchers have described similar methods of iodine speciation analysis [13–17]; however, none have achieved the high resolution, particularly with respect to speciated ^{129}I, within natural samples as is demonstrated in this study. Moreover, the method reported here is unique in that samples require no pre-treatment, as has been discussed by other authors (e.g., [18]). This method may be readily adapted to analyze a wide variety of sample types at concentrations higher than what is required for the current application. Furthermore, the small sample volume (100 µL) needed for speciation analysis is considerably less than that required by traditional chemical speciation separation methods [19] while maintaining high precision at low concentrations. This novel method was tested on a small set of groundwater samples from the Hanford Site.

Experimental

Instrumentation

A Thermo Scientific iCAP RQ™ ICP-MS operating in collision cell (CCT) mode was coupled to a Thermo Scientific Dionex Ion Chromatography System (ICS6000) for iodine speciation measurements (Table 1). This coupled analytical platform is also referred to as an IC-ICP-MS (Fig. 2). The system uses high-pressure ion chromatography (> 2000 psi) to separate chemical anionic species prior to injection into the ICP-MS for isotopic analysis. Background signals for masses 127 and 129 in CCT mode were approximately 1500 cps and 200–400 cps on average, respectively, for the suppressed eluent [50 mM, potassium hydroxide (KOH)] being delivered by the IC to the ICP-MS. By contrast, backgrounds for masses 127 and 129 in standard operation mode yielded intensities of approximately 1000–2000 cps and 10,000–20,000 cps on average, respectively. The inflation of background signal of mass 129 in standard operation mode results from the xenon (Xe) isotope (^{129}Xe) contained within the Ar tank supply to the ICP-MS, and this signal can fluctuate on a day-to-day basis, depending on the volume of Ar remaining in the tank. In CCT mode, research grade oxygen (> 99.998% purity) is used to eliminate > 99% of ^{129}Xe from the Ar supply feed by a charge-exchange reaction, allowing for high precision analysis of ^{129}I, effectively eliminating the daily fluctuations with the ^{129}Xe isobaric interference. To

Table 1 The IC-ICP-MS analytical setup for iodine speciation

ICS6000 parameters	
Sample matrix	0.01% (vol) triethylamine
Eluent (KOH) concentration	50 mM
SP pump flow rate	300 µl/min
External regenerator pump flow rate	360 µl/min
Suppressor current	38 mA
Column compartment temperature	40°C
Sample injection volume (loop size)	100 µL
Guard column	AG-19 4 µm 2×50 mm
Analytical (separation) column	AS-19 4 µm 2×250 mm
iCAP RQ ICP-MS parameters	
Nebulizer uptake	200 µl/min
Cool gas flow	14 L/min
Auxiliary gas flow	0.8 L/min
Sample gas flow	1.02 L/min
CCT gas flow	0.6 ml/min
RF power	1400 W

ensure that Xe has been effectively removed from the analysis and the contribution to mass 129 is solely from iodine, ^{131}Xe is also monitored during all analytical sessions.

The ICS6000 hosts an auto-sampler, injection line system, eluent generator, and chromatographic columns for separation (Fig. 2). Prior to sample injection, the in-line pumps are primed and set at a flow rate of 300 µL/min and left to stabilize for at least 1 h, and the column compartment temperature is set and left to stabilize at 40 °C. The sample is then loaded into an autosampler, and 100 µL is injected by a 250 µL syringe onto a Thermo Scientific Dionex AG-19 IonPac guard column (4 µm 2×50 mm) followed by loading onto a Thermo Scientific Dionex AS-19 IonPac analytical column (4 µm 2×250 mm) (Fig. 2). The AS-19 is a high capacity, hydroxide selective anion exchange column. In-line electrolytic suppression, with the current set to 38 mA, is used to remove the 50 mM KOH from the sample eluent prior to passing through the conductivity detector cell and direct nebulization into the ICP-MS, rendering the carrier solution as water. A bypass of the normal function of the online Anion Electrolytically Regenerated Suppressor (AERS) of the ICS6000 was required due to the diversion of the sample containing effluent to the ICP-MS for trace level iodine analysis. To mitigate the loss of necessary membrane hydration (which typically occurs by recycling the electrolytically suppressed sample solution), an external regenerator (regen) pump supply of water was installed to regenerate the AERS membrane (Fig. 2). This external pump water supply flow is maintained at a level ~ 20% higher than the flow rate of the internal pump (360 µL/min) on the ICS6000 to maintain a slight positive back pressure on the system (Table 1). Following chromatographic separation of the desired anionic
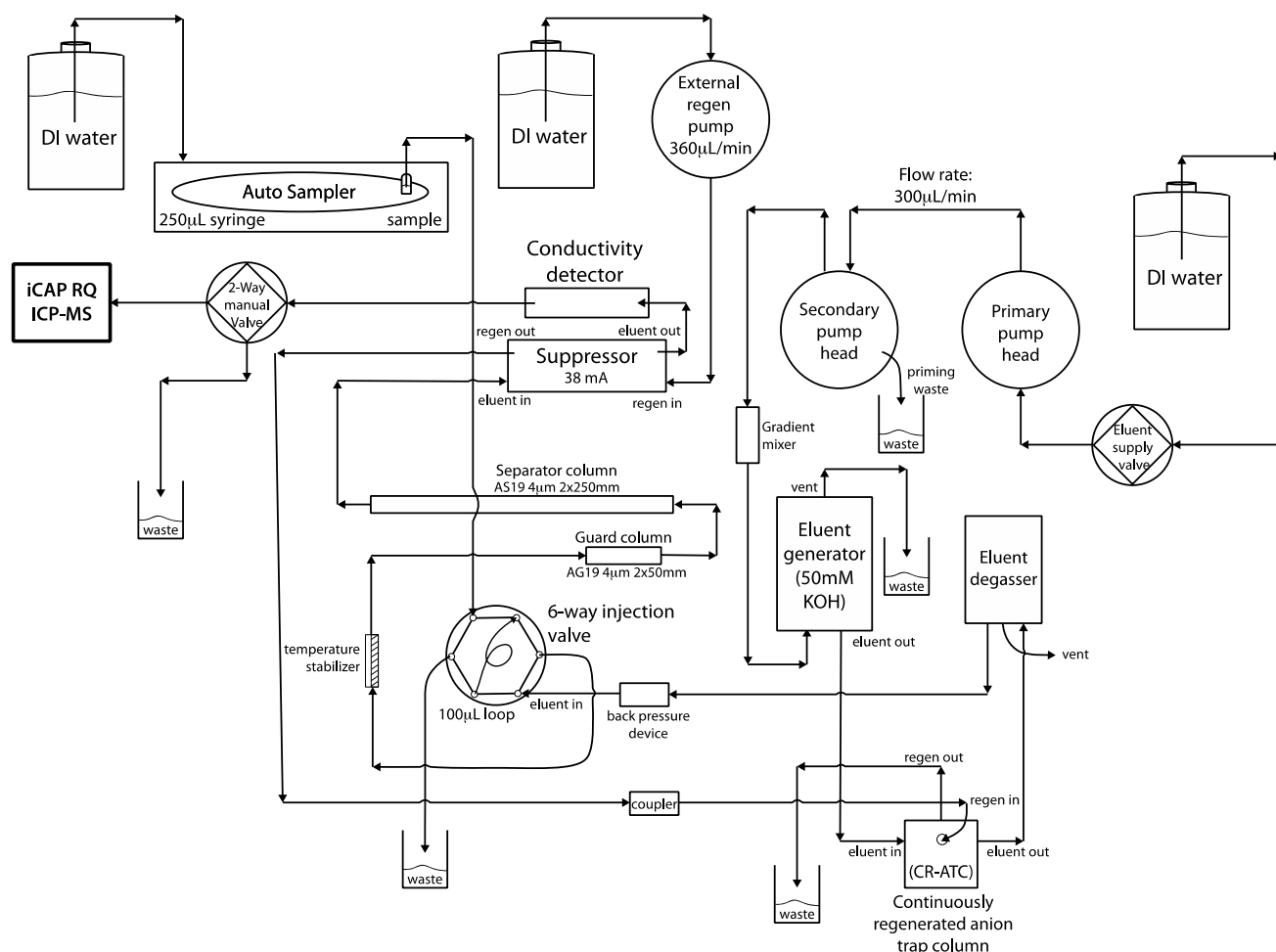
Fig. 2 The IC-ICP-MS instrumental setup. Arrows denoted the direction of fluid flow. See main text for more details

species, the sample is delivered to the ICP-MS and analyzed for isotopics using a time-resolved analytical method, with a total analysis time of < 15 min. Peak retention times of the desired anionic species are mapped using pure reference materials, and the peak areas of each separated species are integrated, compared to certified reference materials, and converted into concentrations reported as ng/L (Figs. 3, 4). Standard reference materials are detailed in the following section.

Sample and standard preparation

Preparation of iodate-129 standards

Both $^{127}IO_3^-$ and $^{127}I^-$ are commercially available for purchase and were used in this study for calibration standards (High Purity Standards) and independent calibration verification standards (iodate: SPEX CertiPrep and iodide: Inorganic Ventures). Two commercially available $^{129}I^-$ standard solutions were also used in this study for calibration

(Amersham RS-218) and independent calibration verification standards (NIST SRM 4949). There are no commercial entities that currently produce $^{129}IO_3^-$ standard reference materials. As such, this study required the oxidation of commercially available $^{129}I^-$ standards, with quantitative recovery. It has been shown previously that I^- can be quantitatively oxidized to IO_3^- using sodium hypochlorite (NaClO) at pH ≥ 8 (to avoid oxidative loss via volatilization of I_2), followed by being scrubbed of excess oxidant using sodium sulfite (Na_2SO_3). This procedure was based on a method described in Takayanagi and Wong [20].

To achieve quantitative oxidation, a volume of 10 mL containing 100 ng/mL $^{127}I^-$ (High Purity Standards) suspended in 0.1 mM NaOH was treated with 0.053 mL of 0.5% (vol) NaClO, allowed to react for 30 min at room temperature, and then treated with 0.053 mL of 500 mM Na_2SO_3. Fresh reagents were mixed the same day of the oxidation experiment. This 100 ng/mL solution served as the stock for the following analysis. An independent 100 ng/mL $^{127}IO_3^-$ (High Purity Standards) solution
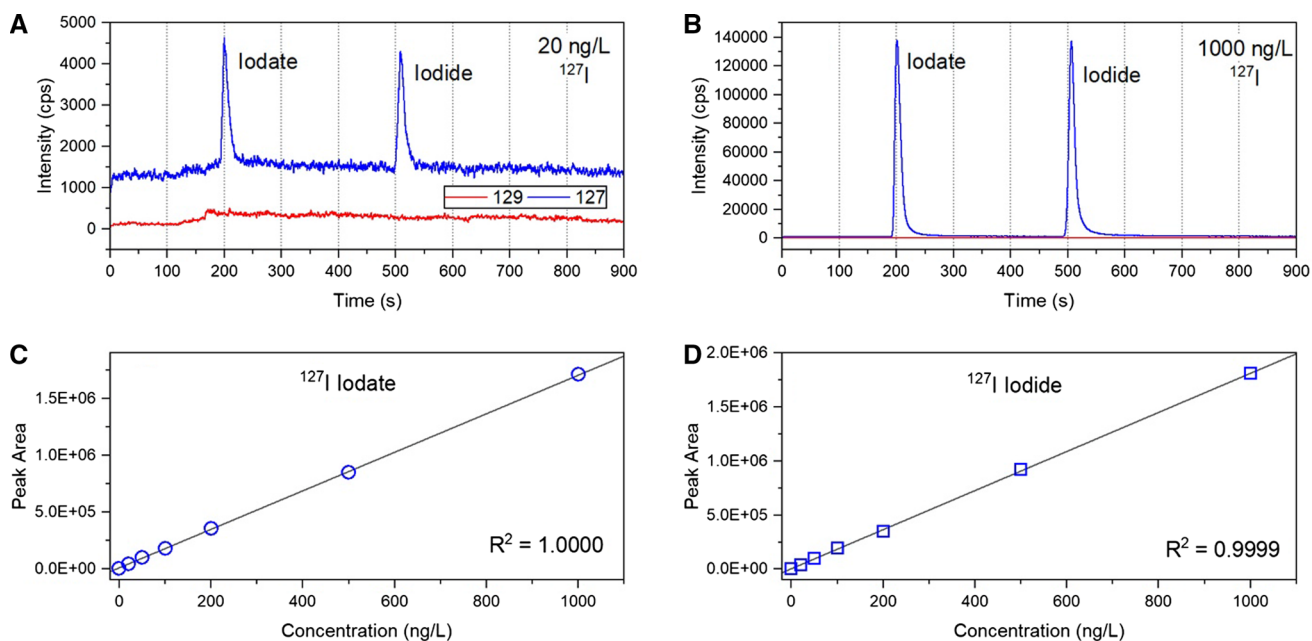
Fig. 3 Speciated ^{127}I calibration using High Purity Standards iodate and iodide. **a–b** 20 and 1000 ng/L calibration standards. **c–d** Species specific calibration curves. Typical calibration range for ^{127}I specia-tion: 20–1000 ng/L with detection limits for iodate and iodide 127 reported as 23.8 ng/L and 24.3 ng/L, respectively
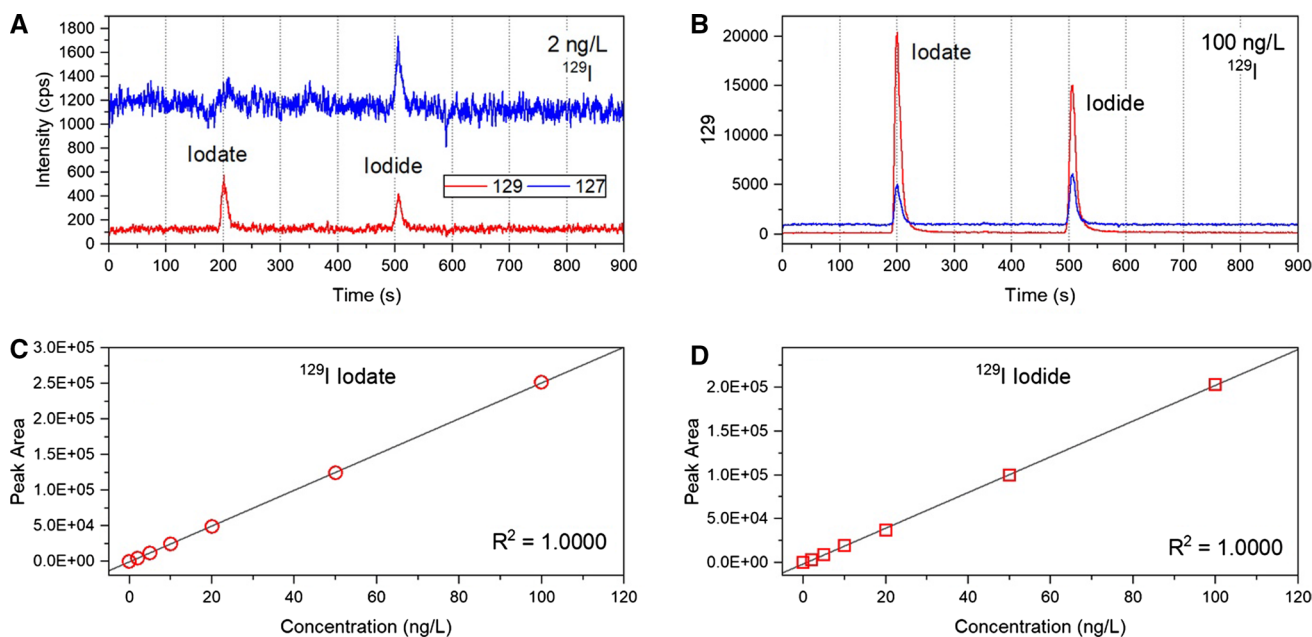

Fig. 4 Speciated ^{129}I calibration with Amersham RS-218 iodide. Iodate was quantitatively oxidized from the certified iodide standard (see main text for details). **a–b** 2 and 100 ng/L calibration standards. **c–d** Species specific calibration curves. Typical calibration range for ^{129}I speciation: 20–100 ng/L with detection limits for iodate and iodide 129 reported as 1.81 ng/L and 2.62 ng/L, respectively. Note the presence of ^{127}I in the Amersham ^{129}I standard, due to this impu-rity, both ^{127}I and ^{129}I are calibrated independently of each other

was also prepared for comparison. All three of the ^{127}I standard solutions, including the newly oxidized ^{127}IO$_3^-$, stock ^{127}I$^-$, and stock ^{127}IO$_3^-$ were diluted to 1 ng/mL, suspended in 0.01% triethylamine (Inorganic Ventures)

to stabilize the iodine species in solution, and analyzed using IC-ICP-MS to compare peak retention times and peak areas. Additionally, the newly oxidized ^{127}IO$_3^-$, and stock ^{127}I$^-$ standards were mixed in equal proportions in

order to assess the $^{127}IO_3^-/^{127}I^-$ peak ratios and confirm unity ($\approx 1 \pm 0.02$).

Following the confirmation of quantitative oxidation of the $^{127}I^-$ standard, the same method was applied to the $^{129}I^-$ standard solutions (Amersham RS-218 and NIST SRM 4949). Both $^{129}I^-$ standard solutions were treated with the previously described quantitative oxidation method in order to create $^{129}IO_3^-$ 100 ng/mL standard stock solutions. Post standard preparation, the IO_3^- solutions were stored in the dark to avoid photodegradation.

Preparation of samples

Groundwater samples were collected from six monitoring wells located within ^{129}I plume areas in the Central Plateau of the Hanford Site (Fig. 1). The sample solutions were kept in cold storage until analysis. Approximately a 0.5–1 mL aliquot from each sample was added to a 1.5 mL glass syringe vial and loaded into the IC autosampler. For analysis, 100 µL was pulled from each sample, injected into the ICS6000 for chromatographic speciation, and directly fed into the ICP-MS for trace iodine analysis, the details of which were described in "Instrumentation" section.

Results

The IC-ICP-MS analytical technique demonstrated well-resolved separation of IO_3^- and I^- peaks with peak retention times spaced > 250 s apart. Speciated standard reference materials yielded detection limits of approximately 23.8 ng/L for $^{127}IO_3^-$ and 24.3 ng/L for $^{127}I^-$. For ^{129}I, the detection limits were approximately 1.81 ng/L for $^{129}IO_3^-$ and 2.62 ng/L for $^{129}I^-$. These levels are well below the federal drinking water standard for ^{129}I and were obtained within a 15-min time frame, using a small sample volume of only 100 µL (Table 2). Standards produced

reliable and reproducible calibrated results for both ^{127}I and ^{129}I species, with retention times for the IO_3^- and I^- peaks separated by several minutes (Figs. 3, 4). Analytical reproducibility was demonstrated by repeated injection of the independent calibration verification standards (described in "Preparation of iodate-129 standards" section) over the course of this work at concentrations of 200 ng/L for the ^{127}I species and 20 ng/L for the ^{129}I species. These injections yielded values for $^{127}IO_3^-$ and $^{127}I^-$ of 202 ± 20 ng/L (2σ, $n = 10$) and 206 ± 20 ng/L (2σ, $n = 10$), respectively. For $^{129}IO_3^-$ and $^{129}I^-$ results yielded 20.2 ± 1.8 ng/L (2σ, $n = 10$) and 18.5 ± 1.8 ng/L (2σ, $n = 10$), respectively. However, analytical methods must demonstrate proficiency when dealing with real samples in order to truly validate performance.

Seven Hanford groundwater samples from wells in ^{129}I-contaminated regions of the 200 East and 200 West Areas (Fig. 1) were selected for ^{127}I and ^{129}I iodine speciation analysis for this study. Splits of the samples had been previously analyzed for total radioiodine concentrations by General Engineering Laboratories (GEL; Charleston, SC). In the GEL method, sodium bisulfite (NaHSO$_3$) is added to an aqueous sample to reduce the total iodine in solution to iodide, and the resulting solution is passed through an anion exchange column to separate and concentrate the iodide. Radioiodine on the resin is then determined by low energy gamma counting (with a detection limit of ~ 6 ng/L). The IC-ICP-MS results demonstrated that nearly all groundwater samples contained ^{127}I in both the iodate (2800–13,500 ng/L) and iodide (28–328 ng/L) species, with the majority existing as iodate. Two samples contained ^{127}I iodide at levels below the detection limit. For ^{129}I, iodate was the only species detected; concentrations ranged from 31 to 130 ng/L (Table 2). The total radioiodine concentration (reported by GEL) showed excellent agreement (average 10% difference) with the ^{129}I-iodate concentration as determined by IC-ICP-MS, which provides an independent validation of the IC-ICP-MS analytical method (Table 2). Observations during

Table 2 Hanford groundwater sample ^{127}I and ^{129}I speciation results using ICP-MS compared to total ^{129}I by radiochemistry methods

Well ID	Sampling date	127 Iodate (ng/L)	127 Iodide (ng/L)	129 Iodate (ng/L)*	129 Iodide (ng/L)	129/127 Iodate ratio	RadChem total ^{129}I (ng/L)	RadChem sampling date
299-W21-3**	2019-06-03	$13,415 \pm 151$ ($n=2$)	84 ± 156 ($n=2$)	129 ± 13.5 ($n=4$)	ND	0.0096	123	2019-06-03
299-E25-43	2020-06-16	5562	88.8	39.4 ± 3.0 ($n=2$)	ND	0.0071	39.4	2020-01-15
299-E25-41	2020-06-29	3528	BDL	31.4 ± 0.7 ($n=2$)	ND	0.0089	36.8	2019-12-06
299-E27-22	2020-06-23	4680	44.1	35.8 ± 3.8 ($n=2$)	ND	0.0077	35.6	2019-09-18
299-E27-13	2020-06-25	2877	BDL	32.1 ± 1.5 ($n=2$)	ND	0.0112	42.4	2020-06-25
299-E27-26	2020-06-23	3494	328	34.3 ± 1.0 ($n=2$)	ND	0.0098	35.8	2019-09-18

*^{129}I speciation was analyzed on two separate dates with errors reported as 2σ ($n=2$ or 4)

**This sample represents two full duplicate samples taken from the same well

BDL Below detection limit, *ND* Not detected

chromatographic separation demonstrated a potential issue with molybdenum (Mo) interfering with the analysis; this is discussed in detail in the following section.

Discussion

Molybdenum interference

Molybdenum anionic species within the groundwater samples at concentrations of several ng/L resulted in phantom 127 and 129 peaks in the ion chromatograms (Fig. 5). Injection tests of groundwater samples into the IC-ICP-MS in both standard mode and CCT while monitoring all stable isotopes of Mo (including ^{95}Mo and ^{97}Mo at natural abundances of 15.9% and 9.6%, respectively) demonstrate that the oxygen in the collision cell of the ICP-MS creates ^{95}MoO$_2$ (mass 127) and ^{97}MoO$_2$ (mass 129) during the analysis,

resulting in false iodine peaks at a retention time between the iodate and iodide peaks (Fig. 5). Fortunately, the anionic Mo species in the sample solution poses no direct interference with the iodate and iodide peak recovery as it conveniently elutes between the two iodine species peaks (Figs. 5, 6). Unfortunately, due to this interference, total ^{129}I cannot be quantified in samples containing Mo concentrations at high Mo/^{129}I ratios (> 20). An attempt was made to develop a mathematical correction for this interference based on the measured response of iodine standards spiked with known amounts of Mo, using the raw intensity of ^{129}I and the % abundances of ^{97}MoO$_2$ and ^{100}MoO$_2$. The correction was effective for single element standards, but it was found to be inadequate for correcting sample ^{129}I concentrations due to the high Mo concentrations and the interactions of other matrix analytes. Molybdenum concentrations in Hanford groundwater are variable, but typical concentrations in the Central Plateau are 2–10 μg/L, which results in a Mo/^{129}I
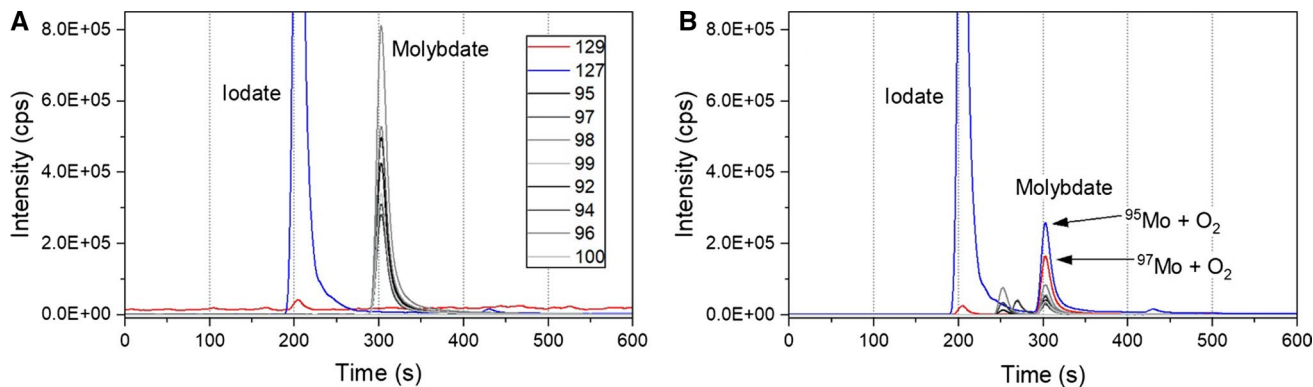

Fig. 5 Test injection of Hanford groundwater sampled from well 299-W21-3. **a** Analyzed in standard (STD) mode and **b** analyzed in collision cell (CCT) mode. All other instrument parameters remain the same. Note the peaks for each mass of molybdenum appearing in STD mode. In CCT mode, the molybdenum peaks diminish and masses 127 and 129 appear in their place, resulting from the reaction of ^{95}Mo and ^{97}Mo with oxygen forming ^{95,97}MoO$_2$ in the collision cell. Fortunately, the instrument generated 127 and 129 peaks do not overlap with iodate or iodide. Molybdate peak retention times are shifted from ~ 450 s (Fig. 6) to 300 s due to the aging of the column. Both guard and analytical columns were replaced and retention times re-mapped prior to analyzing the samples reported in Table 2

Fig. 6 Hanford groundwater sampled from well 299-W21-3, chromatograms for ^{129}I (red trace) and ^{127}I (blue trace). Retention times for iodate are approximately 200 s, for iodide (^{127}I only), approximately 640 s. Molybdate retention time is approximately 450 s. (Color figure online)
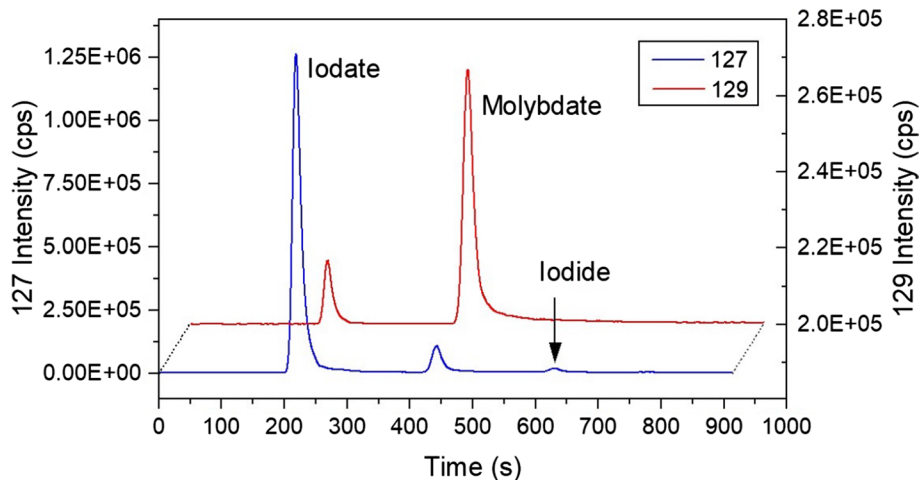
ratio that is significantly higher than our correction could handle. A sample cleanup step that removes Mo would overcome this issue, but such a process would need to be developed for routine use.

Stable and radioiodine speciation in Hanford groundwaters

The first definitive report of stable and radioactive iodine species in Hanford groundwater was published by Zhang et al. [9]. Samples from seven wells in the 200 West Area (Fig. 1) were analyzed by gas chromatography-mass spectrometry (GC–MS) after derivatization to 4-iodo-N,N-dimethylaniline. This methodology enabled the determination of iodide, iodate, and organo-iodine (the latter was calculated from the difference of a total iodine measurement minus the iodate and iodide fractions). Detection limits for both ^{129}I iodide and ^{129}I iodate were 10 ng/L and 14 ng/L (approximately two times higher than the drinking water standard). The new IC-ICP-MS method presented in this study has lower detection limits by a factor of 2–5, requires fewer manual sample manipulations, and requires less sample volume (100 µL). However, the Mo interference discussed previously limits the new method's ability to quantify organo-iodine by difference from total ^{129}I.

Despite limitations in estimating total iodine concentrations, inorganic iodine species are easily quantified using IC-ICP-MS. The method was demonstrated through the analysis of samples from the Hanford 200 West and 200 East Area sites (Fig. 1). In the 200 West Area, well 299-W21-3 (Fig. 1), which has had the highest radioiodine concentrations in the Central Plateau since the well was completed in 2016, was sampled in duplicate (collected at the same time from same well) and analyzed by IC-ICP-MS (Fig. 6, Table 2). Similar to the trends from Zhang et al. [9], iodate was the primary species for both ^{127}I and ^{129}I, the ratio of ^{129}I-iodate/^{127}I-iodate was 0.0096, and no ^{129}I iodide was detected (Fig. 6). Three other studies on 200 West Area groundwater samples provide further evidence that iodate is the predominant form of iodine [6, 21, 22]. However, the speciation information in these latter studies is for ^{127}I only.

In contrast to the 200 West Area, groundwater from the 200 East Area has not been as extensively characterized. Sample results from the five wells analyzed in this study demonstrate similar trends to the 200 West Area. Again, the predominant form of ^{129}I in the groundwater of the 200 East Area is iodate. Iodate ^{129}I concentrations agree very well with the total ^{129}I concentrations as reported by GEL (Table 2). Future analysis of groundwater from wells spatially distributed throughout the 200 East and West Areas using IC-ICP-MS would provide a more complete picture of iodine speciation at the Hanford Site. Coupled with analyses of sediment extracts, these data would help validate fate and transport models that predict plume behavior and serve as the basis for ^{129}I remedy decisions.

Conclusion

A relatively fast (< 15 min), simple, and sensitive method for the low-level determination of both ^{127}I and ^{129}I as speciated iodate and iodide in groundwaters has been developed using only 100 µL of sample. The IC-ICP-MS detection limits for ^{129}I in iodate and iodide species were 1.81 and 2.62 ng/L (0.32–0.47 pCi/L), respectively. Analysis of Hanford groundwater samples yielded iodate as the predominant species for ^{129}I, quantified at values ranging from 31 to 130 ng/L (5.54–23.2 pCi/L), and closely matching total ^{129}I concentrations reported by a radiochemistry method. These results hold promise for the further quantification and speciation of ^{129}I contaminated waters at and below the drinking water standard (5.6 ng/L), with the added potential for isotopic species mapping that could lead to more finely tuned fate and transport studies and informed remediation decisions.

Compliance with ethical standards

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

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