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Automated determination of gallium in seawater using seaFAST pre-concentration and high-resolution inductively-coupled plasma mass spectrometry

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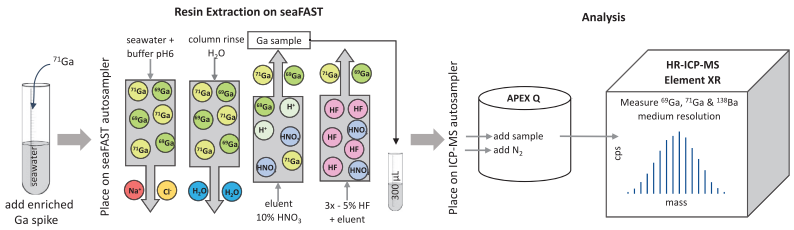
HIGHLIGHTS

- Measuring dissolved gallium in seawater using seaFAST extraction followed by ICP-MS.
- Improved sample volume, detection limits and throughput.
- Isotope dilution addressed sample recovery variability.
- Resolved spectral interferences through analysis in medium resolution on ICP-MS.
- Optimized sample-sample carryover through pre-concentration factor and resin cleaning.

GRAPHICAL ABSTRACT



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ABSTRACT

There has been increased interest in dissolved gallium (Ga) in natural waters due to its long residence time and its usefulness in tracking water masses; however, current analytical approaches are time consuming and labor intensive (e.g., magnesium hydroxide co-precipitation method, ($Mg(OH)_2$)) or have concerns such as carryover and sample recovery (automated resin column extraction). Ocean observing programs, such as GEOTRACES, recover hundreds of samples per expedition. There are both logistical (sample volume) and analytical (person-hour) demands to economically collect and analyze Ga. We present an automated isotope dilution method (using 99.8% enriched ^{71}Ga) to determine Ga in seawater utilizing commercially available equipment while addressing the challenges of a) sample volume and sample pre-concentration factor, b) instrumental interferences, c) sample-sample carryover, d) sample recovery variability, and e) improving sample detection limits, accuracy and precision. A seaFAST SC-4DXS pico (Elemental Scientific, Inc.; ESI) was used to pre-concentrate 20 mL of sample on a Nobias PA1 resin column 67-fold before analysis in medium resolution on a ThermoFisher high-resolution inductively-coupled plasma mass spectrometer (HR-ICP-MS) equipped with an APEX Q FAST enabled spray chamber (ESI) to increase signal intensity and decrease instrument interferences. The new automated seaFAST method reproduced Ga concentrations determined by the $Mg(OH)_2$ method, but with greater precision (RSD

Abbreviations: HR-ICP-MS, high-resolution inductively-coupled plasma mass spectrometer; GF-AAS, graphite furnace atomic absorption spectrometry; RB, reagent blank; PB, procedural blank; $Mg(OH)_2$, magnesium hydroxide co-precipitation method; HCl, hydrochloric acid; HNO_3, nitric Acid; Q-Water, Barnstead E-Pure Water, 18.2 MΩ; HF, hydrofluoric acid; LB, large batch; IS, individually spiked.

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<4%) and a lower detection limit (0.10 pmol L^{-1}). This method is ideal for high throughput applications and can be easily implemented using commercially available equipment.

1. Introduction

In oceanographic research, dissolved trace elements are often studied as proxies for processes such as supply, circulation, and internal - biotic or abiotic - cycling [1]. In recent years, improved analytical methodology has enabled a higher throughput of seawater samples for trace element analysis with increased accuracy and precision [2–8]. However, dissolved gallium (Ga) has remained understudied partly due to analytical challenges including recovery during pre-concentration and instrumental interferences such as doubly charged barium [9,10]. This is unfortunate, since Ga can serve as a less-reactive analogue to aluminum (Al), an element that has been studied extensively in seawater to derive surface ocean dust inputs and thus better constrain the dust supply of iron, a limiting micronutrient in the surface ocean [11–14]. With a longer ocean residence time than Al, Ga provides a temporally-integrated estimate of aeolian dust input to the surface ocean [11,15]. Thus, further study of its distribution could provide greater insight into surface ocean dust inputs and the limiting nutrient iron that is associated with the dust [12–14]. Furthermore, Ho et al. [16] utilized Ga and Al systematics to assess hydrothermal supply, sediment resuspension, and circulation in the equatorial Pacific Ocean. In the Arctic Ocean, Ga has been used as a water mass tracer to deconvolve Atlantic and Pacific Ocean water contributions to the basin [17,18]. However, improved analytical throughput and increased precision is needed to maximize the research potential of the Ga distribution.

The implementation of large-scale oceanic sampling campaigns, such as GEOTRACES [1] (www.geotraces.org), have prioritized mapping of trace elements and their distributions throughout every major ocean basin and have steered sample analysis toward automation. These sampling campaigns can generate hundreds of trace element samples needing analysis at levels of a few pmol L^{-1} to nmol L^{-1} with high accuracy and precision while navigating the large matrix effects of seawater. While work has been done to develop multi-element transition metal methods [3–8,10,19,20], none have successfully automated Ga pre-concentration and analysis with commercially available equipment with improved accuracy and precision compared to previous manual methods [11,21–23].

The high ionic strength of seawater results in matrix effects and interferences requiring the removal of the major salts from the sample. Some of the first methods used to extract Ga and trace elements from seawater used resin-immobilized 8-hydroxyquinoline. The expansion of this resin when moistened is problematic for use in automated systems because the columns are hard-shelled [22,24]. Alternatively, Chelex-100 resin has been used; however, this resin also may swell with added moisture and has poor recoveries for other elements such as manganese making it problematic for multi-element analysis [25]. Newer methods utilize aqueous ammonium hydroxide to form small amounts of magnesium hydroxides ($Mg(OH)_2$) from seawater Mg^{2+} which co-precipitates Ga, as well as many other trace elements [15,16,18]. The $Mg(OH)_2$ method, however, is time consuming, labor intensive, and requires significant hands-on sample manipulation.

Regardless of the extraction method, all require Ga to be pre-concentrated to achieve sufficient sensitivity. The pre-concentration factor required is dependent on the instrumentation. Early studies using resin-immobilized 8-hydroxyquinoline determined Ga by graphite furnace atomic absorption spectrometry (GF-AAS) [23]. While analysis with GF-AAS yields good results, the inherent sensitivity of the instrumentation results in a need for high pre-concentration factors (e.g., 700:1) and thus large volumes of sample water need to be processed (0.25–10 L) [11,21,24]. More recently, high-resolution inductively--coupled plasma mass spectrometer (HR-ICP-MS) has been the preferred analytical instrumentation due to increased sensitivity and lower sample volume requirements [22,25–27].

To analyze Ga by HR-ICP-MS, Ga needs to be isolated from spectral interferences such as $^{138}Ba^{++}$ on $^{69}Ga^{+}$ and $^{55}Mn^{16}O^{+}$ on $^{71}Ga^{+}$ [28]. This can be done procedurally by differential extraction/elution or with increased mass spectral resolution. Analyzing samples in medium resolution (MR; $M/\Delta M \sim 4000$) instead of low resolution (LR; $M/\Delta M \sim 300$) by HR-ICP-MS can resolve these spectral interferences. However, analysis in MR requires increasing the pre-concentration factor to achieve sufficient sensitivity (usually through increased sample volume). For example, studies using 7 mL of sample and pre-concentrating with the ($Mg(OH)_2$) method have analyzed in LR to achieve sufficient sensitivity [15,16,18]. However, while much of the Ba is removed in the $Mg(OH)_2$ sample preparation, a Ba interference still occurs and must be monitored to ensure the quality of the Ga analysis. One way around this issue has been to increase sample volume (50 mL) to obtain a sufficient pre-concentration factor with the $Mg(OH)_2$ method to utilize MR [27]. However, with any sample volume, the $Mg(OH)_2$ method still results in rapid HR-ICP-MS sensitivity reduction due to salt buildup on the ICP-MS cones, which makes high throughput difficult.

Herein, we outline methodology to extract and analyze Ga in seawater utilizing a commercially available extraction and pre-concentration system (seaFAST; Elemental Scientific, Omaha, NE, USA (ESI)). Preparation of seawater samples for HR-ICP-MS analysis using the seaFAST system has become common in recent years [5,10,29], yet has not been adapted to address the specifics of Ga analysis. The method described herein utilizes only commercially available equipment, which reduces the amount of hands-on sample manipulation and potential inter-laboratory data discrepancies. This method resulted from our exploration of ways to eliminate the problems outlined above. Those seeking to develop new seaFAST methods or those interested in determining Ga using lab-made extraction systems may also find the insights herein useful.

2. Methods

2.1. Sample collection

Seawater samples were collected from three separate oceanographic campaigns through the US GEOTRACES program in the Pacific and Artic Oceans (Pacific Ocean cruises GP16 and GP15 and Arctic Ocean cruise GN01). Seawater samples were collected using a trace metal clean rosette equipped with contaminant-free Go-Flo bottles [30]. Samples were filtered through pre-cleaned 0.2 μm filters (Acropac 200 or Supor; Pall Corp.) and collected into 125 or 250 mL acid-cleaned HDPE bottles and stored in double layered plastic zipper bags. Upon return to the lab, samples were acidified to pH < 1.8 with 6 N ultrapure hydrochloric acid (HCl, Optima, Fisher) and allowed to sit for a minimum of one month prior to analysis. These methods follow GEOTRACES standards which are detailed in Cutter et al. (2010).

2.2. seaFAST Reagents and materials

The seaFAST requires several reagents (recipes are provided by ESI), including high-purity Q-water (distilled/deionized, Barnsted E-pure, 18.2 MΩ), buffer, and eluent, plus an acid wash for rinsing the loop and sample probe (Fig. 1). The Q-water, buffer, and eluent were kept in acid-cleaned fluorinated ethylene propylene (FEP) bottles to reduce trace element leaching which was observed when factory-supplied polypropylene bottles were used. For the buffer, ~250 g of ultra-pure glacial acetic acid (Optima, Fisher) was added to ~300 mL of Q-water in a 1 L

bottle, followed by ~300 g of clean ammonium hydroxide. Ammonium hydroxide was made in-house by bubbling ultra-high purity gaseous ammonia through Q-water until saturated. The buffer was allowed to cool and pH was adjusted to 7.0 ± 0.2 using acetic acid and ammonium hydroxide. For the eluent, 160 g of ultra-pure concentrated nitric acid (HNO_3, Optima, Fisher) was added to ~700 mL of Q-water and filled to 1 L to make a 1.7 mol L^{-1} HNO_3 solution. The seaFAST uses two 4-L bottles of HNO_3 acid wash for rinsing the probe and sample loop (Fig. 1). To prepare the wash solution, 56 g of HNO_3 (Optima, Fisher) was added to each 4 L bottle of Q-water (0.6 mol L^{-1}). In addition to the required reagent list provided by ESI, our Ga method requires a 5% hydrofluoric acid (HF, Optima, Fisher) solution for cleaning the column after each elution (Fig. 1). CAUTION: HF readily penetrates skin, causing damage to deep tissue and bone. Users should become familiar with HF precautions before working with this material. In addition to the reagents, two Nobias PA-1 chelate columns (CF-N-0200, 200 μl, ESI) are needed.

2.3. Sample preparation

To prepare samples for seaFAST analysis, a 30 mL aliquot of sample was transferred using an acid-rinsed, metal-free pipette tip into a 50 mL acid-cleaned polypropylene tube in a laminar flow bench. Sample tubes were cleaned with 10% HCl (ACS grade), heated at 60 °C overnight and allowed to cool for 24 h before rinsing 5 times with Q-water. To prepare samples for isotope dilution, an aliquot of an isotopically-enriched ^{71}Ga spike (99.8%; Oak Ridge National Laboratories) was added to each sample prior to seaFAST extraction to achieve an optimal ^{71}Ga:^{69}Ga ratio of ~18 based on expected sample Ga concentrations. This ratio is the geometric mean of the natural isotope ratio of the sample (^{69}Ga, 60.1%, ^{71}Ga, 39.9%) and the isotope ratio of the enriched ^{71}Ga spike (^{69}Ga, 0.2%, ^{71}Ga, 99.8%). This ratio has been shown to be the optimal analytical ratio for minimizing error in isotope dilution analysis [31]. Samples were vortexed 3 times before loading into the seaFAST autosampler. After analysis on the HR-ICP-MS, we calculated the Ga concentration of the sample based on the measured ^{71}Ga:^{69}Ga ratio (sample + spike), the ^{71}Ga:^{69}Ga ratio of the spike, and the natural abundance ^{71}Ga:^{69}Ga ratio.

2.4. Automated pre-concentration and matrix removal

Samples were loaded on a commercially available seaFAST system (SC-4 DX seaFAST pico; ESI) operated in offline mode for pre-concentration and matrix removal (Fig. 1). The seaFAST pico was equipped with original factory supplies including a 6 position autosampler with standard rack, a 4-syringe manifold for dispensing reagents (12, 3, 3, and 3 mL) and a three-valve manifold (5, 11, and 11 ports) for directing samples and reagents (Fig. 1). Samples were loaded onto a 10 mL loop via vacuum and pushed through the Nobias PA-1 chelate sample extraction column with Q-water dispensed from the 12 mL syringe (syringe 1, 2600 μL min^{-1}). The system was configured to mix buffer (syringe 2, 650 μL min^{-1}) into the samples, adjusting the sample pH to ~6.0, prior to passage through the extraction column. The buffer was cleaned by passage through a separate Nobias PA-1 chelate column, henceforth referred to as the cleanup column, prior to mixing with the samples. Because this system was configured with one 12-mL syringe, the sample extraction process was repeated 2 times for a total of 20 mL of sample passed through the extraction column. Note that 30 mL of sample was loaded into the seaFAST autosampler, but only 20 mL went through the extraction column. This was the result of a few mL of sample being lost during each fill of the sample loop. Residual sample matrix and buffer were washed off the column by dispensing 12 mL of Q-water (syringe 1) at a speed of 2500 μL min^{-1} prior to column elution. The first few μL of eluent contained significantly more buffer with a higher pH when the column was rinsed with buffer and Q-water than when rinsed with only Q-water. Since the elution volume for Ga was only 300 μL, it was important to remove as much buffer as possible prior to elution to prevent salt buildup on the HR-ICP-MS cones during analysis. We found no change in Ga recovery when only Q-water was used to rinse the column. This differs from the recommended factory setting for transition metals and rare earth elements, which rinses the extraction column with both Q-water and buffer. A Q-water only rinse has the additional advantage of minimizing use (and cost) of ultra-pure buffer. The elution volume was kept to a minimum of 300 μL to provide a

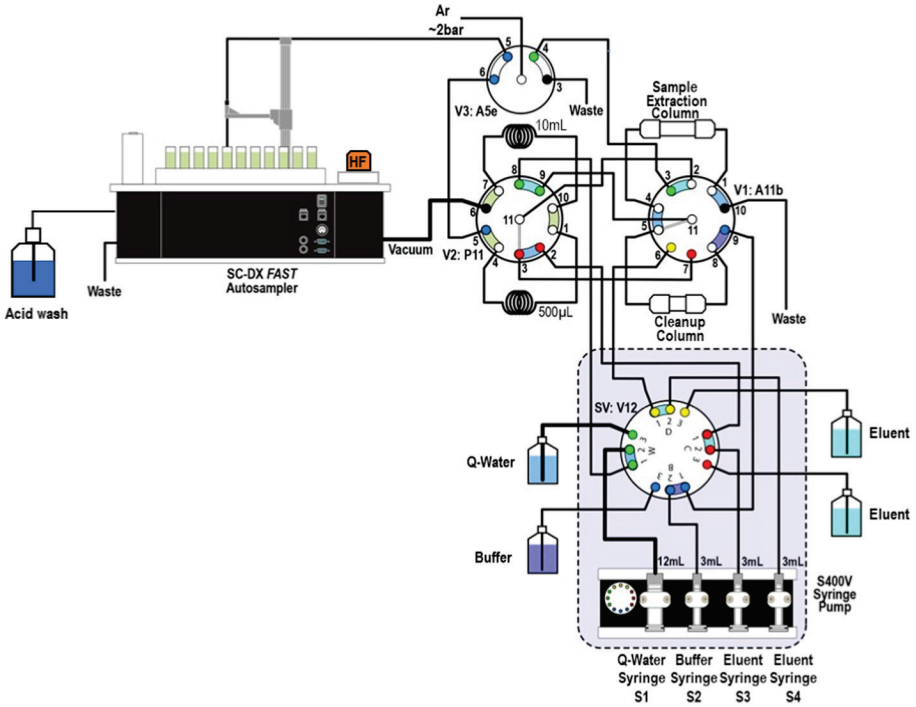

Fig. 1. Schematic flow diagram of the seaFAST valve and syringe manifolds. Figure was adapted from figure provided by Elemental Scientific Inc., Nebraska, USA.

pre-concentration factor of 67-fold. Eluted samples were capped and stored no longer than 3 days to prevent potential sample evaporation.

Column cleaning between samples was more rigorous than the factory recommendations due to Ga's high affinity to the resin. A 5% HF solution was added to the autosampler standard rack, taken up via vacuum into the small 500 μl loop, and was pushed through the sample column via the eluent syringe (syringe 3, Fig. 1). Once the eluent syringe finished pushing the HF through the sample extraction column, the remainder of eluent in syringe 3 (2.3 mL) was dispensed through the sample extraction column for additional cleaning. At the same time, a full syringe of eluent from syringe 4 was dispensed through the system for additional cleaning. We found it necessary to repeat this HF column rinse three times to ensure minimal carryover of Ga between samples. We note that although the HF was pushed through the system via syringes, it at no time came in contact with the quartz syringes, as it was loaded into the 500 μL rinse loop via autosampler vacuum. In contrast to the seaFAST waste, it was important that the sample eluent does not contain 5% HF, as it can damage the seaFAST's quartz syringes as well as the HR-ICP-MS quartz torch. The total time to prepare one sample was ~30 min.

2.5. HR-ICP-MS measurement parameters

Samples were analyzed on a ThermoFisher Element XR HR-ICP-MS with an APEX Q FAST desolvating nebulization/spray chamber system (ESI), and SC-2-DX autosampler equipped with a single syringe pump (ESI). The syringe pump allows for precise small volume sample loading into the HR-ICP-MS inlet system thereby limiting sample volume needed to achieve the desired pre-concentration factor. To further reduce the pre-concentration factor, the APEX Q was used to increase signal intensity by 2 to 4-fold compared to other inlet systems such as the Peltier-cooled PC3 spray chamber (ESI). Another benefit of the APEX Q was the reduction of the $^{55}Mn^{16}O^{+}$ interference with ^{71}Ga. The $^{55}Mn^{16}O^{+}$ interference was determined to be negligible, as a 100 nmol L^{-1} Mn solution yielded an interference of 0.01% in LR and a 0.008% interference in MR (i.e., ^{71}Ga:$^{55}Mn \times 100$). Samples were analyzed in MR to avoid the $^{138}Ba^{++}$ interference with ^{69}Ga in LR (2–5%, i.e., ^{69}Ga:$^{138}Ba \times 100$). Although samples prepared via seaFAST did not retain much Ba (typically <0.5%), enough remained in the eluted samples and interfered with Ga in LR due to the 10^3-10^4-fold concentration difference between these elements in seawater. In MR, the $^{138}Ba^{++}$ interference was determined to be negligible (0.03%) by analyzing a 10 nmol L^{-1} Ba solution. Although the Ba interference was negligible, Ba was still monitored during the run. Specific instrument parameters are shown in Table 1. Note: a PC3 spray chamber was also tested and results were acceptable with interferences remaining low. However, the PC3 yielded HR-ICP-MS signal intensities approximately one third that of the APEX Q.

Table 1
Specific HR-ICP-MS parameters for Ga analysis in seawater.

Parameter	
Resolution	Medium
Cool gas flow (L min^{-1})	16.0
Auxiliary gas flow (L min^{-1})	0.65-0.71
Sample gas flow (L min^{-1})	0.67-0.70
Additional 1 gas (L min^{-1})	0.08-0.09
Nebulizer	APEX (ESI)
Injector	Quartz (1.5 mm)
Spray Chamber	APEX Q FAST enabled (ESI)
Nebulizer uptake rate (μL min^{-1})	175
RF Power (W)	1250
Sensitivity (0.5 ng L^{-1}, In-115, cps)	2-4 x 10^6
Runs	3
Passes	11
Samples per Peak	15
Sample dwell time (ms)	10
Total Sample Time (s)	58
Skimmer Cone	Ni (T1002A-Ni, Spectron)
Sampler Cone	Ni (T1001-Ni, Spectron)

3. Results and discussion

3.1. Blanks, carryover and detection limits

Two types of blanks were analyzed. A reagent acid blank (RB) was eluent (10% HNO_3 v/v or 1.7 mol L^{-1} HNO_3) taken directly from the eluent reagent bottle the day of analysis and analyzed to verify negligible contamination: typically, the RB accounted for ^{69}Ga counts equivalent to <0.1 pmol L^{-1} Ga as well as <0.1% of the ^{71}Ga spike counts. This was also the matrix used for the natural and enriched isotope standards. The second blank was a procedural blank (PB) in which the sample loop was filled only with air; this air "sample" was eluted from the seaFAST in the same way as a sample. By using air and not Q-water for the PB, we eliminated the possibility of our blank value being high due to contaminated Q-water. The PB verified manifold, and column contamination as well as carryover between samples as it was prepared after clean pH 1.8 Q-water and after samples. Both RBs and PBs were monitored over time for increasing counts. Sample extraction and cleanup columns were changed when PB values reached approximately 3-times the PB counts of a new column. Resin reusability was not a concern as we were able to prepare more than 1000 samples using one column (see section 3.2). Although PBs were typically slightly higher than RBs, PBs generally accounted for less than 0.5% of ^{69}Ga and 0.2% of ^{71}Ga total counts and were subtracted during data processing.

Sample to sample carryover [10] was addressed and tested with four independent methods.1) Rinsing and cleaning the column three times with 5% HF between each sample was determined to be necessary. A less concentrated HF solution with fewer rinses were tested during method development but did not clean the column sufficiently after a high Ga sample (~50 pmol L^{-1}). 2) During the latter stages of method development, PB's were prepared after a high Ga sample (~50 pmol L^{-1}) and after cleaning the column with two pH 1.8 Q-water aliquots (same pH as samples). Counts for PB's were similar (typically <2-times) after both a clean column and a high Ga sample indicating little to no carryover. 3) To further verify that high concentration samples did not yield carryover during method development, we analyzed natural Ga amended seawater, amended with a natural Ga addition, over several days ($n = 12$, 6 days) as well as several times in a row ($n = 4$) during one run. For samples measured during one analytical run we achieved a consistent isotope ratio (^{71}Ga:^{69}Ga) with a standard deviation of 0.02 as well as a consistent concentration (48.5 ± 0.2 pmol L^{-1}), demonstrating little to no carryover from the previous sample. In addition, the values from one analytical run were not statistically different from the samples analyzed over several days (49.4 ± 1.1 pmol L^{-1}) as determined by a one-way ANOVA at the $p < 0.05$ level [$F(1,14) = 2.53$, $p = 0.116$]. 4) Additionally, carryover was examined by comparing the ^{71}Ga:^{69}Ga ratio of non-spiked samples prepared on the seaFAST to a natural Ga standard not prepared on the seaFAST. During 25 subsequent analytical runs, non-spiked samples prepared on the seaFAST had a ratio of 0.72 ± 0.04 ($n = 39$) and the natural Ga standard had a ratio of 0.70 ± 0.01 ($n = 39$). To understand how much sample concentrations would be affected in terms of the ratio described above, we consider an example. Analysis of a 38.0 pmol L^{-1} sample with a ^{71}Ga:^{69}Ga ratio of 18 would decrease by 0.2 pmol L^{-1} if the ^{71}Ga:^{69}Ga ratio increased by 0.02. Lower concentration samples would be affected less than higher concentration samples. For example, a 15.7 pmol L^{-1} sample with a ^{71}Ga:^{69}Ga ratio of 18 would decrease by only 0.1 pmol L^{-1}.

To determine the detection limit, a "Ga-free" sample was created by stripping a seawater sample of Ga using $Mg(OH)_2$ co-precipitation and saving the Ga-free supernatant. Some of this Ga-free seawater was amended with natural Ga to ~1 pmol L^{-1} and enriched ^{71}Ga was added to achieve a target ^{71}Ga:^{69}Ga ratio of 18. Both Ga-free and ~1 pmol L^{-1} amended samples were analyzed seven times to determine whether

there was a statistical difference between them. This test was performed using the $Mg(OH)_2$ method as well as our seaFAST method (2 loop fills, 30 mL sample). The $Mg(OH)_2$ method yielded a detection limit of 3.1 pmol L^{-1}, (3 × SD of Ga free seawater) with no statistical difference between the Ga-amended and non-amended samples ($p = 0.7$). For the automated seaFAST method, replicate analyses of the ~1 pmol L^{-1} sample yielded a standard deviation of 0.03 pmol L^{-1} and a detection limit of 0.1 pmol L^{-1}. Ga-free and ~1 pmol L^{-1} amended samples were statistically different ($p = <0.001$) for the automated seaFAST method. We also repeated the seaFAST method detection limit test using only one fill of the 10 mL loop (rather than two, see section 2.4); this adjustment was made to better compare the detection limit to the $Mg(OH)_2$ method, which uses lower sample volumes. The detection limit with only one loop fill (i.e., 10 mL sample extracted on the column) was 0.7 pmol L^{-1} with a statistical difference ($p = <0.001$) between the Ga-free and 1 pmol L^{-1} amended samples (Table 2). Previous methods have used anywhere from 7 mL to 10 L of seawater to achieve detection limits ranging from 0.5 to 3.1 pmol L^{-1} (Table 2). The automated seaFAST method presented here used a minimal amount seawater (30 mL) while improving the detection limit by almost an order of magnitude compared to other similar methods (Table 2) [23,32].

3.2. Recovery and precision

Apparent Ga recoveries from the seaFAST sample extraction column were calculated from the ratio of Ga in the extracted sample (^{71}Ga counts second^{-1} per pmol L^{-1}) to the ratio in a Ga standard (^{71}Ga counts second^{-1} per pmol L^{-1}) that was not extracted on the seaFAST. We call this an apparent recovery since the seaFAST syringe volume delivery was not calibrated and the matrix of the extracted samples were slightly different from the standards due to residual ions in the samples. We observed that within one analytical run (72 h of seaFAST prep, ~110 samples and 1 day of HR-ICP-MS analysis) the recovery could vary by approximately 10% or more from sample to sample. The run-to-run variability was significantly greater than within one analytical run, with new columns giving an apparent 100% recovery, while older columns (i.e., columns having extracted >1000 samples) showed recoveries of 50% or lower, implying the need to change the sample extraction column.

We addressed this low, but sufficient, recovery in two ways. First using isotope dilution, spiking samples with ^{71}Ga prior to loading the column, produced an accurate concentration regardless of variable sample recovery. Sample spike equilibration time varied from a few minutes to 24 h prior to column extraction; however, this did not affect the results (see section 3.5). Second, although HR-ICP-MS sample counts were reduced due to low total Ga recovery, sample counts were sufficient in all analyses since the method is optimized with a high preconcentration factor and the APEX Q spray chamber (ESI), which increased instrument sensitivity.

To further address variable Ga recovery we used standard addition spike recovery test on a large batch seawater sample, where seaFAST column extraction was followed by HR-ICP-MS analysis. An aliquot of ^{71}Ga was added to two batches of the same seawater and one was amended by adding natural Ga. This equates to the original sample concentration being greater than 5 pmol L^{-1} and the final amended concentration being less than 50 pmol L^{-1}; these considerations will yield enough counts to be well over the detection limit and minimize the potential for carryover. Spike recoveries were calculated by subtracting Ga concentrations of the non-amended Ga solutions from Ga concentrations of the amended solutions. To verify recoveries and run-to-run consistency, this sample pair was analyzed at least once during each daily HR-ICP-MS analytical run. For the 32 times the pair was analyzed over 18 analytical runs, the average recovery of the natural Ga spike was 101 ± 2.2%. Therefore, although we observed variable Ga column extraction efficiencies, this did not affect the Ga isotope ratio. By utilizing isotope dilution we negated the issue of non-quantitative Ga extraction.

We investigated the precision of the method several ways (Table 3). First, two large batch samples (10.9 and 20.2 pmol L^{-1} Ga) were pre-spiked with an appropriate aliquot of ^{71}Ga and analyzed repeatedly during one analytical run as well as over multiple analytical runs. Both approaches yielded a standard deviation of 0.3 pmol L^{-1} (Table 3). Additionally, different bulk Pacific Ocean surface (14.4 pmol L^{-1} Ga, sample ID: 13609) and deep water (29.0 pmol L^{-1} Ga, GP15, sample ID: 13455) samples collected on the GP15 cruise were analyzed repeatedly in multiple analytical runs, with the sample aliquots being individually spiked with ^{71}Ga shortly before seaFAST extraction, yielding standard deviations of 0.5 and 1.1 pmol L^{-1}, respectively. The seaFAST method produced a relative standard deviation (RSD) of 3–4% for individually spiked samples, which was much better as compared with an RSD of 7% or more using the $Mg(OH)_2$ method [15]. GEOTRACES coastal (GSC-93, 6.7 ± 0.2 pmol L^{-1}, n = 2) and GEOTRACES Pacific (GSP-29, 14.1 ± 0.1 pmol L^{-1}, n = 2) reference waters were also analyzed; however, due to volume constraints they were only analyzed twice.

To ensure run-to-run consistency, the ^{71}Ga spike concentration was determined for each analytical run using the reverse isotope dilution method. To do this, a standard was prepared with a known concentration of natural Ga and a known volume of ^{71}Ga spike. With a known amount of natural Ga, the known isotope ratios of the enriched spike and natural sample, and the measured ^{71}Ga:^{69}Ga ratio of the mixture, the concentration of the enriched ^{71}Ga spike solution was calculated. To evaluate the impact of the varying ^{71}Ga:^{69}Ga ratios (see section 2.3), we analyzed standards with isotope ratios of approximately 8, 18, and 28 at both the beginning and end of each analytical run. Over the course of 16 analytical runs, we determined that the calculated ^{71}Ga spike concentration (22.1 nmol L^{-1}) averaged about 1.0% lower for the low ratio (^{71}Ga:^{69}Ga = 8) ^{71}Ga spike determinations than for the high ratio determinations (^{71}Ga:^{69}Ga = 28). However, the relative uncertainty of the ^{71}Ga spike concentration within each ratio group was typically 2.3%,

Table 2
Detection limits of this study compared to detection limits reported from other studies with HR-ICP-MS or AAS analysis. All studies listed used HR-ICP-MS unless noted with AAS (atomic absorption spectrophotometer) in the method column.

Source	Detection Limit (pmol L^{-1})	Method	Sample Volume
This Study	0.1	seaFAST resin extraction	30 mL
This Study	0.7	seaFAST resin extraction	13 mL
This Study	3.1	$Mg(OH)_2$	7 mL
King, 2013	1.4	resin extraction	Variable
Middag et al., 2015	1.19	resin extraction	40 mL
Orians and Boyle, 1993	0.5	resin extraction	2 L
McAlister and Orians, 2012	0.24	resin extraction	1 L
Orians and Bruland, 1988	1.3	resin extraction/ AAS	2–10 L

Table 3
Gallium concentrations (pmol L^{-1}), standard deviations (SD, pmol L^{-1}), and percent relative standard deviation (RSD, %) of a large batch (LB) and individually spiked (IS) seawater sample during one run and multiple runs.

Sample Type	Approach	Ga (pmol L^{-1})	1 SD (pmol L^{-1})	RSD (%)	Count
Large Batch	One run	20.2	0.3	1.3	5
Large Batch	Multi Run	10.9	0.3	2.7	33
Individually-spiked	Multi Run	29.0	1.1	3.9	40
Individually-spiked	Multi Run	14.4	0.5	3.2	39

which indicates that uncertainty from varying isotope ratios is less than the analytical uncertainty and can be considered negligible. This indicates that a wide range of isotope ratios will yield reliable results.

3.3. Data comparison

To verify our seaFAST method produced results equivalent to the Mg $(OH)_2$ method previously used, several comparisons were made. First, a selection of seawater samples from GEOTRACES western Arctic Ocean section GN01 (n = 40) that had been analyzed with the $Mg(OH)_2$ method (Mar., 2017–Dec., 2018) [18] were re-analyzed with the seaFAST method (Oct. 25, 2018). Samples for the seaFAST method were taken directly from the bottle used for the $Mg(OH)_2$ method and were chosen for their large range of Ga concentrations (5.6–36 pmol L^{-1}), their vertical distribution in the water column (1–3780 m), and included two full profiles (Supplemental Fig. 1). There was good agreement between the two methods determined by an r value of 0.991 and a p value of <0.001 (Fig. 2). A reduced major axis regression analysis yielded a slope of 1.01 ± 0.02 and an intercept of 0.23 ± 0.43. Two samples (Ga >30 pmol L^{-1}) in our analysis were notably higher in the seaFAST analysis than the $Mg(OH)_2$ analysis (Fig. 2); the variation is not from column carryover (see section 3.1). Isotope ratios of the samples were also verified for both methods and determined to be within the acceptable window (8–28 for seaFAST method, 12–23 for $Mg(OH)_2$ method). All of our standard checks were verified, however; we did not have enough sample to rerun the analysis, so it was unclear why these two samples deviated from the expected trend.

In addition, results from the seaFAST and $Mg(OH)_2$ methods were compared at a GEOTRACES South Pacific crossover station sampled on two different cruises, five years apart. The station, at 10.5° S and 152° E, was first sampled on the 2013 GEOTRACES GP16 (Equatorial Pacific Zonal Transect; EPZT) cruise ($Mg(OH)_2$ analysis, Fig. 3) [16] and subsequently on the 2018 GEOTRACES GP15 (Pacific Meridional Transect; PMT) cruise (seaFAST analysis, Fig. 3). Comparison of these two profiles demonstrate that both methods generate comparable data with surface concentration near 10 pmol L^{-1}, increasing concentration with depth, and deep-water concentrations of about 30 pmol L^{-1} (Fig. 3). The PMT seaFAST profile was much smoother than the EPZT profile, which was likely due to the improved detection limits and reproducibility of the method compared to the $Mg(OH)_2$ method. Although direct comparison

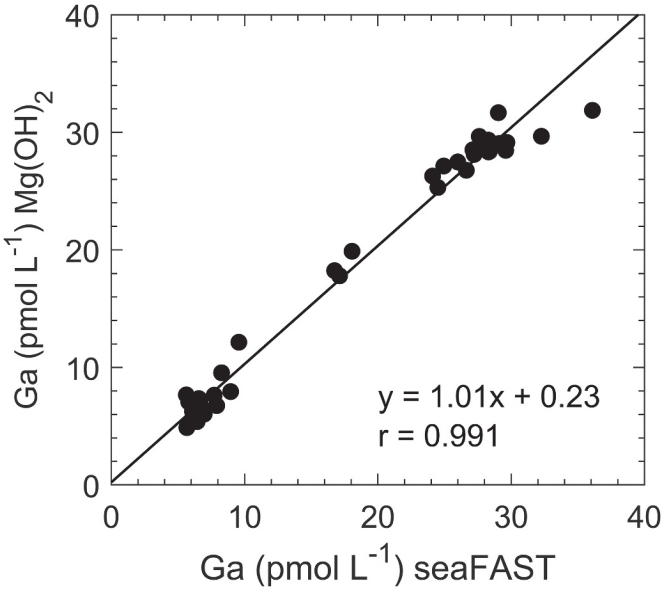

Fig. 2. Gallium concentrations (pmol L^{-1}) from the magnesium hydroxide co-precipitation method ($Mg(OH)_2$, y-axis) compared to the automated seaFAST method (x-axis) (n = 40).

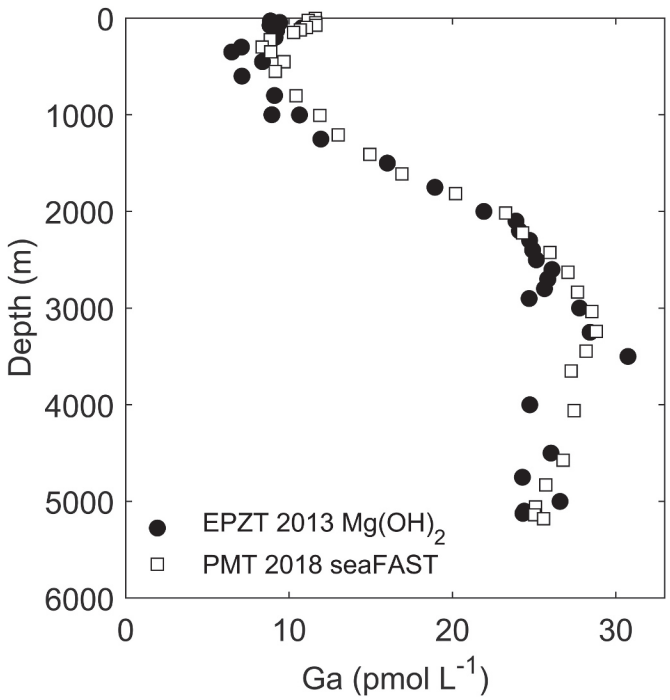

Fig. 3. Gallium concentrations (pmol L^{-1}) versus depth (m) from GEOTRACES crossover station at 10.5° S, 152° E. EPZT (GP15, 2013) station 36 was analyzed using the $Mg(OH)_2$ method (closed circle) and PMT (GP16, 2018) station 35 was analyzed using the new automated seaFAST method (open square).

of the profiles (i.e., a one-to-one plot – see Fig. 2) is not possible since the samples were collected multiple years apart and at slightly different depths, we estimated concentrations at EPZT depths using an interpolated PMT (seaFAST) profile. A spline interpolation (MATLAB) was performed on the PMT seaFAST Ga profile because it was smoother than the EPZT profile (Supplemental Fig. 2). The interpolated PMT data was matched to the corresponding depths of the EPZT Ga profile and a regression analysis was performed (Supplemental Fig. 3). A reduced major axis regression of the EPZT data with the interpolated PMT data (y = 0.95 ± 0.02x + 2.02 ± 0.47) demonstrated a significant relationship (r = 0.990; p-value = <0.001). There was a slight offset of the data at low Ga concentrations, which are observed in the upper 1000 m of the water column (Fig. 3) and may be from temporal variability perhaps associated with changing dust input.

3.4. Low concentration and low volume samples

The method outlined above was designed specifically for seawater samples and can be applied across the entire range of oceanic concentrations with improved results from previous methods. However, in some regions of the ocean, sample concentrations are quite low, in some cases <5 pmol L^{-1}. In these instances, it was possible to increase the pre-concentration factor to 100-fold by extracting a total of 30 mL (3 × 10 mL) of sample and eluting the usual 300 μL. Note, because of some sample uptake loss in the seaFAST system, this method requires 40 mL of sample even though only 30 mL is extracted. We observed no sample-sample carryover using 100-fold pre-concentration for samples less than 15 pmol L^{-1}, so long as the usual HF rinsing protocol was followed between each sample (see section 2.2).

For samples where <30 mL was available, a 33-fold pre-concentration was tested. This variation used a total sample volume of 13 mL with a pre-concentration volume of 10 mL (i.e., an extraction loop of 10 mL, and one loop fill). To improve data quality with such a low pre-concentration, instrument sensitivity was increased from 2–4 × 10^6 cps (0.5 μg L^{-1} In) with the inlet system described above (Table 1) to 2–5 ×

10^7 cps (0.5 μg L^{-1} In) with a nickel jet sampler cone (Spectron, T2001J-Ni) and a nickel X skimmer cone (Spectron, T1002X–Ni). The standard deviation of seven consecutively measured 1–2 pmol L^{-1} Ga samples was 0.3 pmol L^{-1} for 33-fold pre-concentration and 0.03 pmol L^{-1} for 66-fold pre-concentration samples. The diminished reproducibility was due to lower pre-concentration factor as well as diminished instrument stability (despite increased sensitivity) with the jet and X cones. Due to the higher RSD, lower instrument stability and decreased sample counts of the 33-fold pre-concentration, we suggest that these instrument settings/alterations be utilized for samples over ~5 pmol L^{-1}.

3.5. Reproducibility

Finally, we investigated the reproducibility of the seaFAST method. After analyzing more than 1300 samples from the Pacific Ocean over 14 separate runs (Sept., 2019–Feb., 2021), we re-analyzed 73 samples (Feb., 2021) over a large concentration range (2–30 pmol L^{-1}) and achieved excellent reproducibility (Fig. 4). A correlation analysis yielded an r value of 0.994 and a p value of <0.001 indicating the data are significantly correlated (Fig. 4). Reduced major axis regression yielded a slope of 1.02 ± 0.01 and an intercept of −0.30 ± 0.23 demonstrating reproducibility between the first and second analysis with the seaFAST method. In addition, sample-spike equilibration times were randomized between a few minutes and 24 h for both preparations. Thus, no significant difference in Ga concentrations was observed within the 24 h spike equilibration time.

4. Conclusions

The need for automated determination of trace metals is growing with global programs such as GEOTRACES that produce thousands of oceanic samples. Previous attempts to automate Ga sample extraction have had mixed success, as memory effects and reproducibility prove challenging [10]. However, our seaFAST method successfully reduces sample volume requirements and increases precision and reproducibility compared to previous methods. Our automated method for determining Ga in seawater uses commercially available equipment, thereby reducing labor costs, human error, and laboratory expertise. Our method addresses the five major challenges of analysis.

1) Sample volume and sample concentration factor; due to the seaFAST's ability to automate and consistently elute small volumes of sample, an initial sample of only 13–40 mL is required to achieve a 33-100-fold pre-concentration factor depending on the expected sample concentration or available volume.
2) Instrumental interferences; we found spectral interferences for Ga in seawater are negligible when samples are analyzed in MR by HR-ICP-MS with either the APEX or PC3 spray chambers.
3) Sample-sample carryover was addressed by optimizing pre-concentration factors and rinsing the column three times with 5% HF between each sample.
4) Sample recovery variability; the addition of an isotopically-enriched ^{71}Ga spike (isotope dilution method) prior to running the sample through the sample extraction column eliminates column recovery uncertainty.
5) Improved sample detection limits, accuracy, and precision are a byproduct of automation and isotope dilution methodology.

By analyzing both a series of identical samples as well as a GEOTRACES crossover station across a full depth range with both the older $Mg(OH)_2$ method and the new automated seaFAST method, we are able to demonstrate improved precision, accuracy, excellent detection limits, and outstanding data agreement. We are hopeful that the use of commercially available equipment utilized in this method will allow this method to be easily transferable to other laboratories.

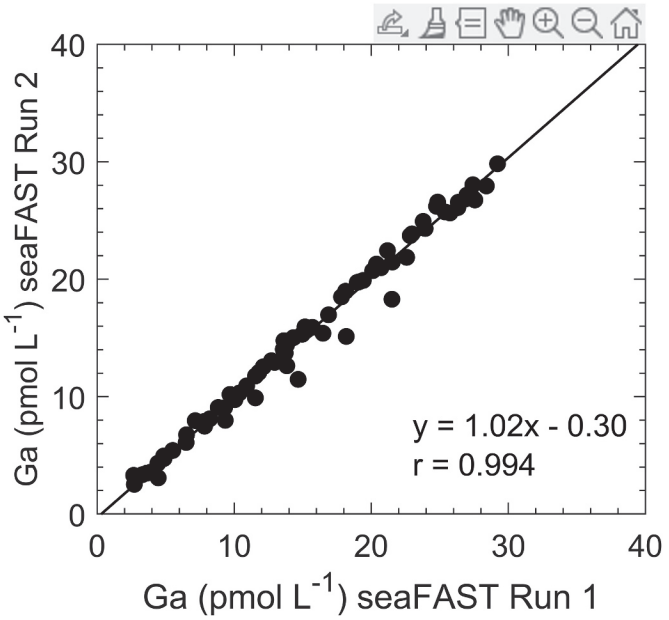

Fig. 4. Gallium (pmol L^{-1}) seaFAST method rerun comparison. seaFAST Run 1 (x-axis, i.e., the first time the samples were analyzed) samples came from 14 separate days of analysis while the 2nd run (y-axis, i.e., the second time the samples were analyzed) data was from the same day of analysis.

CRediT authorship contribution statement

Melissa Gilbert: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft. **Peng Ho:** Methodology, Writing – review & editing. **Laura Whitmore:** Methodology, Data curation, Writing – review & editing. **Alan Shiller:** Funding acquisition, Data curation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2023.340799.

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