

1 The Present and Potential Future of Aqueous Mercury Preservation: A Review

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7 Abstract

8 Mercury is considered to be one of the most toxic elements to human health. Due to pollution from
9 industry and artisanal gold mining, mercury species are present globally in waters used for agriculture,
10 aquaculture, and as drinking water. This review summarises methods reported for preserving mercury
11 species in water samples and highlights the associated hazards and issues with each. This includes the
12 handling of acids in an uncontrolled environment, breakage of sample containers, and the collection
13 and transport of sample volumes in excess of 1 L, all of which pose difficulties to both *in-situ* collection
14 and transportation. Literature related to aqueous mercury preservation from 2000 – 2021 was
15 reviewed, as well as any commonly cited and relevant references. Amongst others, solid-phase
16 extraction techniques were explored for preservation and preconcentration of total and speciated
17 mercury in water samples. Additionally, the potential as a safe, *in-situ* preservation and storage
18 method for mercury species was summarised.

19 The review highlighted that the stability of mercury is increased when adsorbed on a solid-phase and
20 therefore the metal and its species can be preserved without the need for hazardous reagents or
21 materials in the field. The mercury species can then be eluted upon return to a laboratory, where
22 sensitive analytical detection and speciation methods can be better applied. Developments in solid
23 phase extraction as a preservation method for unstable metals such as mercury will improve the
24 quality of representative environmental data, and further improve toxicology and environmental
25 monitoring studies.

26 1. Introduction

27 1.1. Background (Mercury in the environment)

28 Mercury (Hg) is ubiquitous in the environment and is one of the most toxic elements to human health,
29 being described as one of the 13 priority hazardous substances under the Water Framework Directive.
30 Concentrations in drinking water are restricted to just 2 µg L⁻¹ total Hg for acute poisoning¹ and a
31 tolerable intake set at 2 µg total Hg kg⁻¹ body weight per day². Both acute and long-term exposure to
32 the metal can result in severe, irreversible neurological and developmental complications, commonly
33 referred to as Minamata disease. It is therefore one of the most widely studied and monitored
34 environmental pollutants. There are three main species of Hg found in natural waters: inorganic
35 mercury (Hg²⁺), elemental mercury (Hg⁰), and organic species such as methylmercury (MeHg⁺) and
36 dimethylmercury (Me₂Hg). These species are often highly mobile³ and their most significant
37 environmental interactions are shown in Figure 1. Making up 1-40 % of the total Hg fraction, MeHg⁺ is
38 considered the most toxic Hg species. Organic Hg species are highly bioaccessible and prone to
39 bioaccumulation. For example, predatory fish can have up to 10⁶ times higher concentrations of total
40 Hg than the surrounding waters, with 95 % of this being methylmercury⁴. Total aqueous Hg
41 concentrations are usually less than 10 ng L⁻¹ Hg in uncontaminated natural freshwaters, with polluted
42 waters generally being defined as higher than 100 ng L⁻¹ and even being reported at over 50 µg L⁻¹ Hg¹,
43 ⁵⁻⁷. Monitoring total Hg and speciation data is vital to prevent human and environmental exposure to

44 harmful concentrations of the metal. Due to the naturally low concentrations of total and speciated
 45 Hg, sample pre-treatment and preparation are vital to ensure accurate and precise measurement with
 46 appropriate detection limits. Many preservation and preparation techniques for Hg recommend
 47 filtration of the water sample. Dissolved Hg concentrations may adsorb to particulate matter over
 48 time, altering the measurable dissolved concentration and posing different analytical challenges⁸⁻¹⁰.
 49 The potential for toxicity of particulate-bound Hg is not well researched^{11, 12}, with toxicity studies
 50 focusing on dissolved species concentrations. For speciation analysis, sample pre-treatment methods
 51 should generally avoid inter-species conversion, to provide representative species data of the sample.

52 1.2. Preservation and storage: importance and challenges

53 Preventing losses of Hg from water samples has been an ongoing problem for many years¹³⁻¹⁵. Safely
 54 preserving and storing Hg concentrations in water samples is particularly difficult. Many species are
 55 unstable in water, with total Hg (Hg_T) concentrations can show losses of >70 % within 1 week^{13, 15}.
 56 Elemental Hg^0 is volatile in solution and so readily escapes from uncapped samples or into any
 57 container headspace^{13, 16}. Inorganic Hg^{2+} is the most stable species in solution but is still prone to losses
 58 through sorption to the container walls or reduction to the less stable species Hg^0 ^{13, 17, 18}.
 59 Methylmercury and other organomercurials can undergo photolytic reduction to Hg^0 and can adsorb
 60 to container walls, as well as minor losses occurring from coagulation with humic acids^{13, 18, 19}. Any loss
 61 of Hg from the sample or contamination of the sample will produce erroneous results and limit the
 62 usefulness of the data, especially for samples used in environmental monitoring and human health
 63 studies.

64 Wall-sorption of Hg has been extensively studied in the past^{10, 13, 15, 17, 20-22} and the choice of sample
 65 container material has been noted as a major factor in mitigating this. Glass and PTFE containers are
 66 preferred for sampling Hg in waters, as wall sorption is greatly reduced in these materials⁸. However,
 67 PTFE is relatively expensive when compared to other materials such as polyethylene, as demonstrated
 68 in **Error! Reference source not found.** Glass containers are heavier and will become hazardous should
 69 breakage occur. Polyethylene (PE) and polypropylene (PP) are relatively more affordable alternatives
 70 than PTFE or glass, are often used in water sampling⁹ and are more robust than glass containers, but
 71 can pose a significant risk of Hg loss if the sample is untreated^{15, 22}.

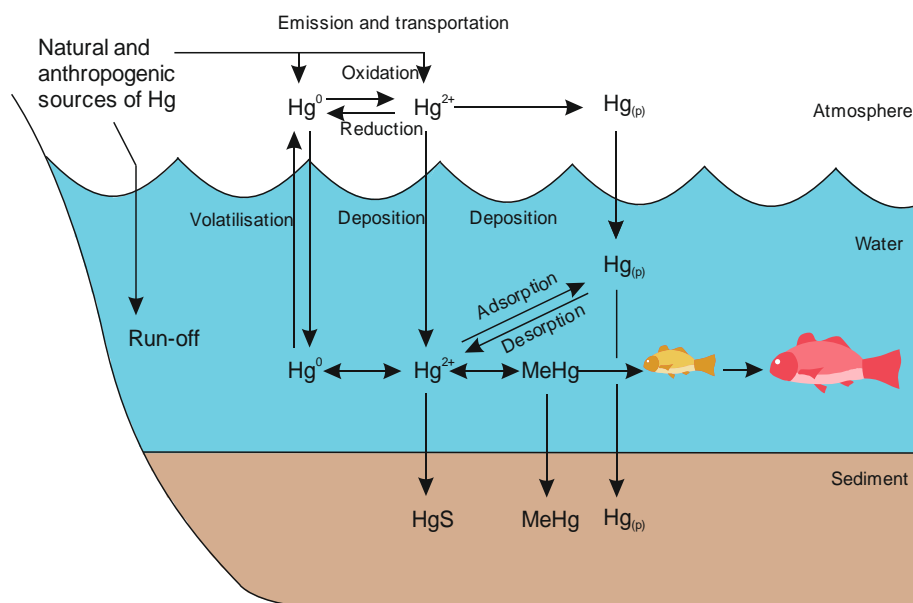
72 *Table 1 Approximate price comparison of container materials from online suppliers (sourced from FischerScientific on 4th*
 73 *March 2022)*

Container material	Approximate price per 100 mL sample bottle*
High density polyethylene (HDPE)	\$1.50
Polypropylene (PP)	\$2
Borosilicate glass	\$1
Polytetrafluoroethylene (PTFE)	\$40

* Prices are obtained from online vendors (SigmaAldrich, FischerScientific) and converted from GBP (£) to USD (\$) (4th March 2022)

74

75 1.3. Scope of the Review and Methodology



76

77 *Figure 1 Biogeochemical cycle of mercury in the environment. Species described: Elemental mercury, Hg⁰; inorganic mercury,*
 78 *Hg²⁺; methylmercury, MeHg; particulate bound mercury, Hg(p); mercury sulfide, HgS (Adapted from Kim and Zoh (2012)³)*

79 The aim of this review was to critically assess the current literature related to the sampling,
 80 preservation and storage of Hg samples during transport from field to laboratory, to improve the
 81 likelihood of obtaining representative concentration and speciation data.

82 For the current preservation and pre-treatment methods, key benefits were highlighted and
 83 limitations associated with the different methods were considered. Using ScienceDirect literature
 84 database, Scopus, the WorldCat Library database and NERC library services, peer-reviewed, published
 85 literature from 2000 to 2021 was reviewed using the search terms “mercury”, “water” or “aquatic”,
 86 and “preservation”, “storage” or “speciation”. Literature that involved the preservation and storage
 87 of aqueous Hg was reviewed. Any papers that were frequently cited throughout the reviewed
 88 literature were also assessed and included if relevant. The benefits of the preservation methods were
 89 explored, and any hazards associated with *in-situ* use and transportation were highlighted. The current
 90 applications of solid-phase extraction (SPE) in Hg analysis were examined and the potential benefits
 91 of the sorbents for sampling and preservation were explored. For solid-phase methods, the search
 92 terms “mercury”, “preconcentration” or “speciation” or “removal” or “recovery”, “water” or “aquatic”
 93 were used, and similarly any common and relevant references were assessed and included. Some key
 94 considerations of the reviewed SPE methods were: the retention of the target analyte, the recovery
 95 of the analyte upon desorption, and the compatibility of the desorption method with analysis
 96 techniques.

97 A summary of literature on the preservation of Hg and its species by addition of a reagent is given in
 98 **Error! Reference source not found.** and a summary of literature on the solid-phase extraction of Hg
 99 and its species is given in **Error! Reference source not found.2.**

100 2. Current trends for field measurement, sampling and preservation

101 2.1. Field measurements

102 Analysis of analytes and their species *in-situ* eliminates the need for preservation and reduces the risk
 103 of inter-species conversion and loss of analyte over time, providing a more accurate representation of
 104 real-world chemistry. However, there is a greater risk of sample contamination and a greater difficulty

105 maintaining appropriate analytical conditions, due to a lower control over the environment when
106 compared to a laboratory.

107 Commercially available field probes have been developed for *in-situ* Hg²⁺ stripping voltammetry
108 analysis. These are reported to measure Hg²⁺ in the field with detection limits of 5 µg L⁻¹, as well as
109 other trace and transition metals. For pristine waters, these probes will likely struggle to produce an
110 accurate quantitative result as mercury concentrations can be as low as 1 ng L⁻¹ Hg²⁺. Rocha et al.
111 (2019) reported detection limits of 5 µg L⁻¹ Hg²⁺ in river water using a portable analyser²³, unsuitable
112 for the WHO guideline value¹ of 2 µg L⁻¹ Hg but may be useful for indicating severe Hg pollution. A
113 similar detection limit was reported by Bhardwaj et al. (2020) in pond and drain water²⁴. Gold
114 nanoparticle electrodes have been developed by Hwang et al. (2021) for Hg²⁺ determination, achieving
115 detection limits of 1.7 µg L⁻¹ Hg²⁺ with a linear response between 10-100 µg L⁻¹ in landfill leachates²⁵.
116 This highlights the ability for these technologies to be used in difficult matrices, however detection
117 limits are currently unsuitable for speciation analysis or for Hg concentrations found in most natural
118 waters.

119 Other methods of Hg field analysis use headspace Hg vapor analysers, relying on the evolution of
120 elemental Hg vapour from water samples²⁶. These probes have been reported to achieve detection
121 limits of approximately 0.09 µg L⁻¹ Hg⁰, but are designed specifically for Hg concentration in air;
122 preparative chemicals are required for other matrices to evolve Hg vapour and the data must be
123 converted to other units for comparison to other analysis methods and water studies^{1, 5-7}.

124 **2.2. Acidification**

125 As field measurement of Hg in natural waters is not currently possible, preservation of the dissolved
126 metal is vital for Hg analysis. Recommended methods for preservation of Hg in natural water samples
127 generally follow the guidance of other trace metals, namely acidifying water samples with nitric
128 (HNO₃), hydrochloric (HCl), or sulphuric acid (H₂SO₄)⁸⁻¹⁰. The choice of acid is important for Hg stability;
129 the use of HNO₃ has been found to still be susceptible to large losses of Hg from water samples through
130 both volatilisation and sorption to container walls^{13, 15, 17, 27}.

131 Hydrochloric acid is recommended as a suitable preservation method for dissolved Hg species in
132 freshwater samples²⁰. Inorganic Hg²⁺ can complex with chloride ions to form the stable HgCl₂ complex,
133 and tri- or tetra-chloromercury complexes if the chloride concentration is further increased^{21, 28}. These
134 are more stable in solution than other species and are not co-precipitated by metal oxides and
135 hydroxides²⁹⁻³¹. A 1 % (v/v) HCl solution was reported to prevent loss of Hg²⁺ over 55 days in 500 mL
136 HDPE containers²⁸. The lower pH and the presence of chloride ions increases the stability of Hg²⁺, as
137 demonstrated by the preservative abilities of HNO₃ (6% v/v HNO₃) for Hg in seawater reported by
138 Gardner and Gunn (1997)³² and 20 mg L⁻¹ NaCl + 0.15% (v/v) HNO₃ for Hg in deionised water reported
139 by Louie et al. (2012)²⁸.

140 These conditions also increase the stability of MeHg in water samples. In a 0.5% (v/v) HCl solution
141 stored in Teflon containers at 1-4 °C in the dark, MeHg is reported to be stable for up to 250 days in
142 both freshwater and seawater¹⁰. Sulphuric acid has also been recommended for the preservation of
143 aqueous MeHg in saline media, as hydrochloric acid (>0.4% v/v) may result in the artificial formation
144 of monomethyl mercury during the distillation and ethylation process typically used for MeHg
145 speciation¹⁰.

146 When considering speciation, Bloom et al.⁵ reported that acidification may alter labile Hg(II) resulting
147 in desorption from particulates in unfiltered samples, oxidation of Hg⁰ or coagulation of dissolved
148 organic carbon and humic acids which can precipitate Hg from solution.

149 3. Solid-phase extraction

150 Solid-phase extraction offers the potential for reagent-free field sampling of Hg from water samples.
151 Sorbents and solid-phase methods are frequently used in the analysis of dissolved Hg for sample
152 preparation and pre-treatment, such as preconcentration³³⁻³⁹, speciation^{34, 36, 37, 40-43} and removal of
153 Hg^{37, 44-49}. Solid-phase extraction was previously studied for retention and stabilisation of heavy metals
154 for analysis at a later date^{33, 50}. Adsorption of Hg to a solid-phase mitigates the risk of loss from wall
155 sorption; there is less chance of contact between an analyte bound to a solid-phase and the container
156 walls when compared to an analyte in an aqueous-phase. This approach has been investigated in the
157 past^{14, 33, 51}, but is not in widespread use.

158 3.1. Thiol- functionalised resins

159 A common approach to Hg-selectivity in sorbents is to exploit the affinity for Hg of thiol-containing
160 compounds; diphenylthiocarbazone (dithizone)^{42, 52, 53}, 2-mercaptoethanol⁵⁴,
161 diethyldithiocarbamate³³, and other compounds have been used to either functionalise resins or for
162 complexation with aqueous Hg. These reagents provided recoveries of inorganic, methyl-, ethyl- and
163 phenyl- species of Hg of over 70 %, with preconcentration factors suitable for aqueous Hg
164 concentrations of between 0.1 – 50 $\mu\text{g L}^{-1}$ ^{33, 42, 54, 55}. While most work focuses on a deionised water
165 matrix, Margetínová et al. (2008)⁵⁴ successfully extracted Hg from natural freshwaters, by complexing
166 Hg with 2-mercaptophenol before passing samples through C18 columns. The use of 2-
167 mercaptophenol as a complexing agent comes with separate risks as the reagent is volatile, has a
168 strong odour, and the concentrated solution is highly toxic, so was reportedly diluted to a 5 mM 2-
169 mercaptophenol solution before use. The high organic concentration of the methanol eluent solution
170 limits the analytical techniques available to this method, relying on HPLC/CV-AAS for speciation
171 analysis.

172 Blanco et al. (2000)³³ achieved a similar extraction by immobilising diethyldithiocarbamate onto
173 homemade C18 microcolumns. The C18 immobilised diethyldithiocarbamate column used a 50 mL
174 sample volume to achieve recoveries of >70 % for Hg²⁺ and >65 % for MeHg⁺ from freshwater river
175 samples, with detection limits of 0.2 $\mu\text{g L}^{-1}$. The diethyldithiocarbamate modified C18 columns showed
176 potential as an in-field preservation method, as samples could be readily passed through the
177 microcolumns in the field and inorganic Hg²⁺ is stabilised for approximately 2 weeks. The detection
178 limits are unsuitable for typical concentrations in many unpolluted natural water samples, primarily
179 being suitable for areas of moderate to high Hg pollution. There was a substantial decline in recovery
180 of MeHg after 2 weeks of storage, even when held at 4°C in the dark³³. Over 85 % of the spiked MeHg
181 could be recovered within 7 days of extraction to the cartridge, declining to <50 % by 14 days. This
182 trend was also seen with Hg²⁺, albeit much less significant with a recovery of 80 % Hg²⁺ after 30 days
183 storage. This method was applied to LC-ICP-MS, allowing for a fraction of the sample volume required
184 from the technique reported by Margetínová et al. (2008)⁵⁴. In addition, the eluent composition (0.5%
185 v/v HCl + 5% w/v sodium thiosulphate) is compatible with a wide variety of analytical techniques, so
186 is suitable for a broader scope of laboratories.

187 Dithizone functionalised C18 columns were developed by Yin et al. (2010) to effectively recovery Hg
188 species from tap water samples (Hg²⁺, MeHg⁺, EtHg⁺)⁴². The method used just 3 mL 100 mmol L⁻¹
189 sodium thiosulphate solution to elute the retained species, from sample volumes of 100 mL. This
190 eluent choice allows a wide variety of analytical techniques to be applied but may show limitations
191 where acidification or oxidation of the sample is required, due to the formation of solid sulphur which
192 may decrease Hg concentrations by formation of solid Hg₂S. Using HPLC-ICP-MS analysis, detection
193 limits of 3 ng L⁻¹ Hg were reported from sample injection volumes of just 20 μL . This work supported

194 by Wang et al. (2022), using a 1% (v/v) 2-mercaptoethanol eluent for elution of Hg species⁵³. This
195 eluent is still compatible with a wide range of analytical techniques with some careful adjustments,
196 such as use of organic introduction systems for ICP-MS analysis for routine use.

197 **3.2. Commercially available chelating resins**

198 Commercially available ion exchange resins have been developed for the removal of Hg from industrial
199 wastewaters; Duolite GT-73™ and AmberSep GT-74™ are examples of these. The recovery and
200 preconcentration of Hg in solution using these resins has been explored as diffusive gradient thin-film
201 cartridges^{35, 45, 56}. Pelcová et al.⁵⁶ reported that both Duolite GT-73™ and AmberSep GT-74™ can
202 remove inorganic, methyl-, ethyl-, and phenylmercury from both tap and river waters with limits of
203 detection between 30 – 50 ng L⁻¹ Hg concentrations. The loading capacities for Hg are often high, >70
204 mg Hg g⁻¹ resin⁵⁷, as these resins were designed for the treatment of wastewaters with high Hg
205 concentrations, often greater than 500 µg L⁻¹. These efficiently and selectively extract Hg²⁺ from a
206 variety of water matrices but some studies reported difficulty in recovery from the resins by elution^{35,}
207 ⁵⁶, instead resorting to either digestion of the resin prior to analysis or direct absorption spectrometry
208 measurement of the resin. From solutions containing up to 100 µg L⁻¹ Hg²⁺, over 92 % of the total Hg
209 concentration could be readily recovered by digestion of the Duolite GT-73 resin™, with negligible
210 losses in the digestion step³⁵. Duolite GT-73™ is now out of production, but AmberSep GT-74™ and
211 other variations of this resin are still available^{56, 58}.

212 **3.3. Cationic exchange resins**

213 As Hg species are predominantly cationic in the aquatic environment, cation exchange resins offer a
214 method to remove these from solution. These resins are effective at removing cationic Hg species such
215 as Hg(OH)₂²⁺ complexes, but there may be issue with the sorption of uncharged complexes and
216 species, such as HgCl₂ or MeHgCl. The conditioned resins are often washed with deionised water prior
217 to extraction, as this decreases the likelihood of forming uncharged or negatively charged Hg
218 complexes in the resin which impede sorption^{21, 28}.

219 A commercially available resin, Dowex 50W X4™, was found to remove inorganic Hg and some organic
220 Hg species from a variety of natural water matrices whilst allowing for elution using 0.1 % thiourea
221 and 8 % hydrochloric acid⁵⁹. Gomez et al.⁶⁰ used the commercially available Dowex Marathon™ cation
222 exchange resin as comparison to activated carbon and treated and non-treated coals. They reported
223 the cationic exchange resin had the best sorption capacity, 98 µg Hg g⁻¹ resin, and recoveries, >95 %
224 Hg²⁺, of the studied sorbents. These experiments used 50 mL sample volume but used a high Hg
225 concentration, between 0.1 – 998.4 mg L⁻¹.

226 Cationic exchange columns have been used for online preconcentration of Hg species in sea waters,
227 achieving detection limits of 42 pg L⁻¹ when using HPLC-ICP-MS analysis⁶¹. This indicates suitability for
228 the analysis of low Hg concentrations in waters. Ion exchange sorbents, columns and cartridges are
229 commercially available and often relatively inexpensive. Some technical knowledge and training are
230 required for field use, but use of hazardous materials is limited in field applications. Other cations
231 present may compete for the active sites of the resin, but high loading capacities would overcome
232 this. Issues may also arise in samples with high chloride concentrations due to the formation of
233 uncharged complexes that would not be retained by the sorbent and pass through to the effluent²¹.
234 Metals are eluted from these columns using strong acids, such as hydrochloric acid. While this is
235 compatible with many analysis techniques, the concentrations of acid may require a dilution and thus
236 reduce the overall sensitivity of the method.

237 **3.4. Polyaniline**

238 Polyaniline is a readily available polymeric sorbent that can be used for removal of metals from
239 aqueous solutions and preconcentration of trace metals. Studies have primarily examined inorganic
240 Hg species by addition of a bulk resin to a water sample, but separation of methylmercury is also
241 possible^{36, 41}. Mercury analyses using polyaniline for preconcentration have achieved 2-3 ng L⁻¹ Hg
242 limits of detection using CV-AAS and FAAS, suitable for uncontaminated natural water and drinking
243 water; these matrices usually show Hg concentrations below 10 ng L⁻¹ ⁶². Mercury has been
244 successfully preconcentrated with polyaniline from a variety of matrices including bottled water, lake
245 and groundwaters, seawater, and even fish tissue using 100 mL sample and 10 mL 0.3 % HCl + 0.5 %
246 thiourea eluent^{36, 41}. The eluent is suitable for a wide range of analytical detection methods, due to
247 the relatively low organic compound concentration and acid concentration.

248 Some polyaniline composites have also been examined for Hg removal, to improve resin stability, Hg
249 selectivity and efficiency of sorption. Polyvinyl alcohol⁶³, humic acid¹⁵, polystyrene⁶⁴, and other
250 reagents have been used to create polyaniline composites, usually with an optimal pH range of 4-7.
251 The predominant Hg species at this pH range is Hg(OH)₂ species, which will form Hg-N bonds with the
252 polyaniline units and other bonds such as Hg-S with the composite molecules. At pH <4 the polyaniline
253 nitrogen may be protonated, reducing the number of possible Hg-N bonds that can be formed.

254 **3.5. Magnetic SPE**

255 In the past decade, developments for solid-phase extraction technologies have incorporated the use
256 of magnetic particles. By functionalising magnetic particles, the sorbent can be added to a sample to
257 sorb Hg and then be readily removed by applying a magnetic field. The selectivity and efficiency of the
258 sorbent is dictated by the functionalisation; some previously used compounds include 1,2-
259 ethanedithiol⁶⁵, 3-mercaptopropyltrimethoxysilane⁴³, 1,5-diphenylcarbazine⁶⁶, and other task-specific
260 monoliths⁶⁷. These have achieved 0.1-100 ng L⁻¹ Hg²⁺ detection limits of inorganic Hg in real-world
261 aquatic matrices such as lake, river water and for spiked tap water. The 1,2-ethanedithiol
262 functionalised particle also adsorbed cadmium (Cd) and lead (Pb) ions from solution with 0.82 ng L⁻¹
263 Cd and Pb limits of detection⁶⁵, making the method more desirable commercially and for heavy metal
264 pollution studies. Song, et al.⁶⁸ synthesised a task specific monolith with vinylboronic anhydride
265 pyridine complex for functionalising the magnetic particles. This was synthesised for magnetic solid-
266 phase extraction microextraction of inorganic Hg²⁺, methyl-, ethyl- and phenyl- Hg. Using the chelating
267 sorbent, recoveries of up to 94 % and detection limits of 20-160 ng L⁻¹ could be achieved.

268 Magnetic solid-phase particles can be readily removed from solution with a magnetic field and can be
269 used to achieve detection limits of <100 ng L⁻¹ Hg. Speciation of Hg²⁺ and MeHg can be achieved and
270 changing functional groups on the sorbent can allow for multi-elemental extraction. The sorbent can
271 be applied to a water sample collected in a container, allowed to sit in the sample for an appropriate
272 length of time, and then the enriched sorbent can be removed using a magnet. Elution from magnetic
273 sorbents is generally achieved using HCl or HNO₃ and thiourea in relatively low concentrations.
274 Analysis is typically conducted using ICP-MS techniques, however the composition of eluent and the
275 preconcentration of the metal make the methods compatible with less sophisticated techniques such
276 as AAS. The main limitation for magnetic SPE is the multi-step synthesis required to produce the
277 sorbent, as the methods used often produce approximately 1 g of sorbent and scaling-up the synthesis
278 has not yet been explored⁶⁵. The product must also be characterised before use to ensure a
279 homogenous and effective sorbent.

280 **3.6. Gold-based SPE**

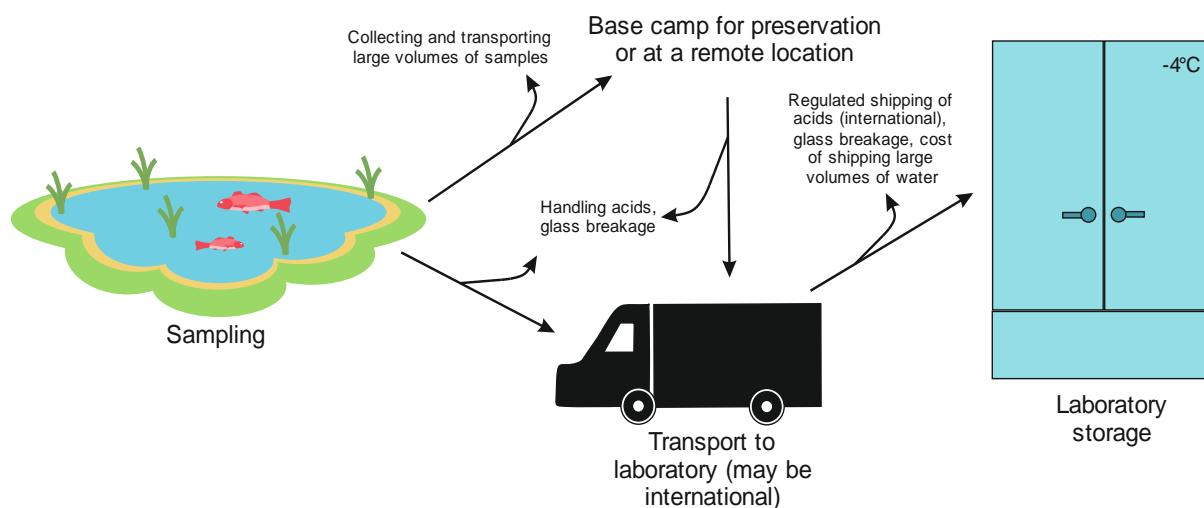
281 Many metals form amalgams with Hg and this property is frequently exploited for solid-phase
282 extraction of Hg vapour. Cold vapour (CV) methods use gold to amalgamate reduced Hg vapour,
283 trapping the analyte in place and allowing release of the preconcentrated Hg by thermal desorption.
284 As the amalgam is formed on the solid particles, problems arising from interferents are often negligible
285 and so can be readily applied to environmental matrices. This has been examined and exploited in
286 the form of gold nanoparticle columns^{38, 69, 70}, greatly increasing the surface area when compared to a
287 bulk solid. Similarly, columns made using gold nanosheets offer a relatively simple method of
288 extracting and preconcentrating aqueous Hg with very good sensitivity, as low as 80 pg L⁻¹ Hg²⁺⁷¹.
289 Schlathauer et al.⁵¹ developed a dipstick of immobilised gold nanoparticles, allowing for a simple field-
290 sampling method that can achieve levels of sensitivity suitable for pristine waters and sea waters. As
291 a simple dipstick, this method is easily conducted in the field without the need for extensive training
292 or technical competency, as well as posing little hazard to the operator or during transport. While
293 technically capable, the cost and complexity of manufacturing the dipstick alongside the need for
294 annealing at 600 °C before each measurement currently prevents this from being easily reproduced.
295 Additionally, gold-based SPE typically uses thermal desorption to liberate Hg from the solid-phase.
296 While this effectively eliminates potential interferences, the detection method becomes limited to
297 those suited for gases and vapors, such as CV-AAS.

298 3.7. Critical review of sample preservation and solid-phase extraction

299 While acidification of water samples for Hg analysis is commonly recommended, the handling and
300 transportation of acids is becoming increasingly more regulated, particularly where controls over
301 health and safety are more difficult, i.e. handling concentrated acids outside of a laboratory setting,
302 and where limitations are imposed for international transportation of acids (**Error! Reference source
303 not found.**). Any handling of acids comes with inherent hazards and risks due to their corrosive nature.
304 This makes preservation methods that require concentrated acids particularly difficult to conduct in
305 the field, as well as for transportation of acids and acidified samples particularly transport by air where
306 regulations are becoming stricter⁷². Historically, oxidising agents were also recommended for Hg
307 preservation⁷³ by oxidising the Hg species to the stable Hg²⁺, however this destroys speciation data
308 and so has fallen out of favour. Other reagent-based methods for preservation show potential, but
309 have not been fully explored¹³. For example, increasing the ionic strength of solution by addition of
310 ionic salts, i.e. NaCl, allows for a less hazardous method to preserve Hg¹⁵, but literature primarily
311 focuses on Hg²⁺ in spiked and synthetic matrices with little assessment of un-spiked water
312 environmental samples. In addition, elevated chloride concentrations can co-precipitate in MeHg
313 distillation and ethylation procedures¹⁰, making the procedure unsuitable for traditional speciation
314 analysis.

315 Due to the importance of Hg speciation analysis for toxicity studies, there is a concern for interspecies
316 conversion and loss of sample integrity during preparation and storage of water samples⁷⁴⁻⁷⁷.
317 Individual samples are often taken for each desired species and preserved using different methods⁷⁸.
318 This approach allows the operator to collect speciation data for Hg, but vastly increases sample volumes
319 required and limits the environments in which Hg studies can be conducted. For example, studies in
320 developing countries and remote areas must ship samples internationally for analysis^{79, 80}. If samples
321 are shipped unpreserved, then speciation data may not be considered as representative of the
322 sampled environment.

323



324

325 *Figure 2 The sampling and preservation process, with key challenges highlighted*

326 Recent developments in SPE for Hg analysis have focused on preparative methods such as online-
 327 speciation and -preconcentration; hyphenating a chromatographic separation to the detection
 328 method to enrich the analyte, improving detection limits and analytical sensitivity. The SPE
 329 preparation methods often operate in a broad pH range, usually optimal at pH 4-7 so suitable for many
 330 natural waters. These methods are often developed for mass spectrometry techniques^{33, 65, 68} and
 331 atomic absorption and fluorescence techniques^{33, 39, 52, 54, 81, 82}, due to their comparatively high
 332 sensitivity for environmental metal analysis.

333 Ion exchange resins sorbents and columns are commercially available and have been shown to sorb
 334 both inorganic and organic Hg species from aquatic media. Chelating resins are the more prominent
 335 choice for Hg sorption in the literature, as the affinity for sulphur allows for selective extraction of
 336 Hg^{33, 42, 53, 54}. Some chelating resins, however, require synthesis or processing to create columns and
 337 cartridges for field use^{33, 42}. Commercially available resins are available but have shown difficulty in
 338 eluting retained Hg species, requiring digestion processes to liberate the adsorbed Hg^{56, 58} which may
 339 affect speciation data through oxidation of the retained species. Cation exchange resins only require
 340 an acid, HCl in this case, and thiourea to efficiently elute Hg⁵⁹, but these may be more susceptible to
 341 competition with other cations in the sample. Typically, ion exchange resins use dilute acids and weak
 342 organic concentrations to elute immobilised Hg species. The eluent composition allows for analysis
 343 using a wide range of instruments and can therefore be applied in most laboratories.

344 Functionalised magnetic sorbents can be added to a collected water sample and then readily removed
 345 by application of a magnetic field, either an electro-magnet or a strong, permanent magnet^{43, 65-67}.
 346 These sorbents are relatively simple to use in the field, with minimal training requirements and a high
 347 Hg extraction efficiency. The eluent can typically be used with a wide variety of analysis techniques,
 348 although some developed sorbents require methanol⁶⁷ which will limit the compatibility of the
 349 methods. The synthesis of these sorbents is often more complicated than other sorbent materials,
 350 and may require work to scale-up synthesis to be viable as a widespread sampling procedure.

351 Gold-based sorbents are some of the most selective and efficient sorbents available for Hg extraction
 352 and preservation, but come with a considerable cost due to the raw materials price^{38, 51, 71}. Therefore,
 353 a high reusability is necessary to offset the cost. Desorption of the retained Hg is conducted via
 354 thermal desorption, which limits the compatible analysis techniques to those which can measure Hg
 355 vapour, such as AAS.

356 Another technology, diffusive gradient thin-film (DGT), was investigated for the sorption and storage
357 of Hg in the field^{56, 83}, with analysis after transport to the laboratory. These are usually deployed into
358 a water source, for example a river or waste treatment water tank, for 4 – 24 hours, where the Hg
359 species become bound to the resin^{58, 84}. For some DGT resins, Hg is irreversibly bound and so must be
360 digested before analysis or alternative analysis methods must be used^{56, 58}. For other resins, Hg species
361 are elutable with either thiourea or HCl the latter being preferable for many analysis techniques and
362 when ethylation of the Hg species is required for MeHg quantification⁸⁴.

363 A current deficiency in literature is the exploration of adequate storage capacities and times for SPE
364 methods (Supplementary Table 2). When investigating sorption of Hg species, there is a tendency to
365 focus on trace metal concentrations, such as $<0.1 \mu\text{g L}^{-1} \text{Hg}^{2+}$ ^{43, 51, 69, 71}. While this is adequate for
366 unpolluted waters, the usefulness of the developed methods for contaminated water samples is in
367 question. Resins developed for Hg removal show comparatively higher storage capacities, often over
368 $10 \text{ mg Hg g}^{-1} \text{resin}$ ^{36, 48, 63-66}, and storage capacities of functionalised columns are dependent on the
369 amount of functionalising agent immobilised on the solid phase^{33, 42, 53}. Storage times are also under-
370 represented in literature, often only being investigated for around 1-week of storage^{33, 42, 51, 53}. Filling
371 this gap in knowledge will provide necessary information for applying SPE as an offline field sampling
372 and preservation method.

373 4. Future perspectives of field analysis and preservation

374 4.1. The future of Hg field analysis

375 Emerging technologies use nanoparticles and colorimetric methods to determine Hg^{2+} in natural
376 waters. Fluorescence probes have been developed for Hg^{2+} determination, for example Kaewnok et
377 al.⁸⁵ developed a [5]helicene-based probe highly selective for Hg^{2+} which can be used as a test-strip
378 with a detection limit of $6.5 \mu\text{g L}^{-1} \text{Hg}^{2+}$. This work requires development for the in-field screening of
379 Hg^{2+} in environmental samples. Rhodamine nanoparticles have been developed for smartphone-based
380 colorimetric analysis, as a method to detect Hg^{2+} in pristine water matrices^{86, 87}. These nanoparticles
381 are highly selective for Hg^{2+} , showing little interference with other metals. Recoveries of over 95 %
382 were reported for both drinking water and dam water with a limit of detection of $1.3 \mu\text{g L}^{-1} \text{Hg}^{2+}$ ⁸⁷,
383 and $0.1 \mu\text{g L}^{-1} \text{Hg}^{2+}$ in spiked deionised water with recoveries $>80 \%$ Hg^{2+} in river and lake water⁸⁶.
384 Lopreside et al. reported colorimetric smartphone detection of Hg^{2+} using an orthogonal paper
385 biosensor⁸⁸. Using three different biotic “reagents”, Hg^{2+} concentrations and toxicity can be evaluated
386 simultaneously. The sensors each determine Hg over different periods of time, between 17 – 60
387 minutes, and with varying limits of detection, $0.58 – 17 \mu\text{g L}^{-1} \text{Hg}^{2+}$. This allows for either quantitative
388 or semi-quantitative analysis, if required. The use of multiple sensors reduces the chance of
389 interference by other compounds and elements in the matrix, however silver and cadmium reportedly
390 inhibit the activity of the sensors.

391 With the prevalence of smartphones and simplicity of use, colorimetric methods are likely to become
392 a mainstay in field analysis methods for trace metals in the future. The biggest challenges to analysis
393 in the field are the limit of detection in relevant matrices, determination of different Hg species and
394 contamination of the sample. While good practice can overcome sample contamination issues, the
395 sensitivity of portable instruments is currently not suitable for mercury concentrations less than the
396 WHO guideline limit of $2 \mu\text{g L}^{-1}$ total Hg, or for speciation analysis. Current field analyses of Hg species
397 are unable to achieve appropriate sensitivity, as Hg species are often found in concentrations $<10 \text{ ng}$
398 L^{-1} particularly in unpolluted sites. The portable instruments tend to favour analysis of Hg^{2+} , neglecting
399 the determination of MeHg and other relevant species. This limits their usefulness for toxicological
400 and monitoring studies, as organic Hg species data is vital for assessing the health impact of Hg

401 concentrations in waters. With these current restraints, analysts must weigh up improved analysis and
402 sensitivity in laboratory measurements versus representative but less accurate data measured in the
403 field.

404 **4.2. Solid-phase extraction as a sampling and preservation method**

405 Solid-phase extraction shows potential as future reagent-free sampling methods for Hg in natural
406 water samples, as columns and microcolumns^{33, 38, 42, 54, 59, 71}, as DGT cartridges^{56, 58}, particles added
407 directly to samples⁴³, or as a dipstick⁵¹. The ability to extract Hg from solution and retain the metal on
408 a solid bed reduces the likelihood of Hg loss over time; volatilisation is reduced due to strong
409 interactions with the stationary phase and wall sorption is reduced as the analyte is immobilised on a
410 solid phase with little interaction with the container walls. By immobilising the analyte to a solid phase,
411 the likelihood of chemical changes is reduced, and speciation data can be preserved^{33, 43, 53}. Most
412 column-based SPE methods are relatively simple to conduct and, once prepared, can be used in the
413 field to extract dissolved Hg without the need for additional reagents. The use of columns and
414 cartridges also eliminate the need for glass containers, reducing hazards from breakages.

415 One promising SPE methods for Hg preservation, gold-nanoparticle dipsticks, are effective at removing
416 Hg from natural water samples⁵¹. The dipsticks can be simply dipped into a water sample, with little
417 knowledge required for field-use, few possible interferents and is a relatively quick method at only 10
418 – 20 minutes per sample. The dipstick must be annealed at 600 °C to ensure gold nanoparticle
419 formation and the synthesis was reported to require a system for depositing a gold vapour to a defined
420 area on the stick. This limits the ability to scale-up production of the dipstick for routine use, however
421 the article reported excellent reusability at 145 cycles of sampling and annealing without performance
422 loss. While offering superb extraction and recovery, the gold-based sorbents are limited to techniques
423 for analysing Hg vapours, such as AAS, due to the requirement for thermal desorption. This may limit
424 the overall usefulness of the technique, as other analysis methods cannot be used as readily.

425 Other sorbents, such as thiol-functionalised sorbents or functionalised magnetic solid-phases, are
426 typically compatible with a wider variety of analytical techniques due to eluent composition. Often,
427 the eluents used are a dilute acid^{33, 36, 43, 59, 63, 65} or a low organic compound concentration^{33, 36, 42, 43, 59,}
428 ⁶⁵, so are not as restricted as thermal desorption. In addition, inorganic and methyl- Hg species were
429 retained and stored on diethyldithiocarbamate immobilized C18 microcolumns for up to 2-weeks and
430 1 week respectively before elution³³, highlighting the potential for reagent-free field sampling while
431 preserving speciation. These columns, microcolumns, and cartridges are simple to use in the field, with
432 minimal training requirements and little-to-no risk to the operator. With high recoveries and readily
433 incorporating preconcentration of Hg species, SPE methods offer the ability to collect and preserve
434 representative Hg concentration and speciation data, while being suitable to many analysis techniques
435 and laboratory settings.

436 The cost of the SPE methods is often higher than that of sample acidification but the reduction in
437 storage space and sample volume, as well as reduced risk to the operator and simpler field-
438 application, offset the cost (Table 2). Preconcentration, usually via SPE, may be required for samples
439 only treated by acidification, so sorbents may already be required. A currently unexplored risk of
440 columns and cartridges is the accumulation of Hg from ambient storage conditions; this is likely
441 mitigated by choice of casing material and appropriate storage, but further work on this is needed.
442 However, avoiding storage in areas of with Hg vapour contamination may make this concern
443 negligible.

444 Another important, yet unresolved issue is the lack of validated *in-situ* analytical techniques that can
445 accurately measure Hg species concentrations. Without the determination of species concentration
446 at the point of collection, interspecies conversion during storage and transportation cannot be fully
447 validated for environmental samples and so speciation data determined in the laboratory may not be
448 representative of the real-world concentrations.

449

450

Table 2 Approximate cost-per-sample of some suggested Hg preservation and solid-phase extraction methods

Preservation/ preparation method	Relevant species	Main costs	Approximate reagent cost per sample*	Sample holding time	Application in the field	Cost-benefit
Acidification (HCl and HNO ₃)	Total Hg, Hg ²⁺ , MeHg	HCl and HNO ₃ divided by samples at 1 %	\$2.50 per 500 mL sample	6-12 months	Addition of 1% (v/v) acid to a collected water sample, either at a base-camp or in a laboratory after shipping	<ul style="list-style-type: none"> + Relatively cheap per sample + Recommended – Separate samples are usually required for speciation techniques (i.e. distillation for MeHg) – Needs to be added to samples when at a base-camp or laboratory, to ensure safety measures – Potential difficulties and regulations in transportation of samples
Thiol-functionalised ion exchange cartridges	Hg ²⁺ , MeHg	Price of cartridges and approximate price of functionalising reagents	\$5 per sample	Not investigated beyond 2 weeks	Water samples are passed through homemade microcolumns or cartridges in the field, transported to a laboratory for elution	<ul style="list-style-type: none"> + Highly selective for Hg and can be filled with water prior to sampling, reducing the amount of hazardous waste in-field. + Can be re-used and regenerated several times, improving cost-effectiveness – Preservation and storage of Hg species has not been fully explored – A time-cost must be considered for preparation of SPE-phases, albeit relatively labour un-intensive
Commercially available resins	Total Hg, Hg ²⁺	Initial price of resin	\$10 per sample	Not investigated	Water samples passed through preprepared DGT cartridges, or applied as a batch sorbent	<ul style="list-style-type: none"> + Selective for Hg in water samples, usually applied for Hg removal in waste-water + High analyte capacity relative to other resins and sorbents – Resins are often expensive (~\$500 for 250g resin) – For a column/cartridge, column loading and preparation time must be considered

Gold sorbents	Total Hg, Hg ²⁺	Price of gold metal for synthesising sorbent	\$5 for sample	Not investigated	A dipstick, which can be dipped into a water sample, or passing water through preprepared microcolumns or cartridges	<ul style="list-style-type: none"> + These offer high levels of reusability (>145 cycles), and Hg desorption can be conducted thermally + Minimal interference/competition for the sorbent, due to selective amalgamation – Synthesis requires controlled sputtering and vapour deposition technologies, which may not be readily available – Gold is an expensive reagent, not readily available in most laboratories for preparation of the columns/dipsticks, therefore has a high initial cost
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*Prices are obtained from online vendors (sigmaaldrich.com, fishersci.co.uk, accessed 21 August 2022) converted from GDP (£) to USD (\$)

451

452 **5. Conclusion**

453 While the mechanisms for dissolved Hg loss have become more well defined over the years, safe
454 methods for preservation, storage and transportation of samples to the laboratory for measurement
455 of both total Hg and individual Hg species still remains a challenge. Different species require separate
456 preservation methods, hazardous or expensive materials, and large sample volumes to improve
457 detection limits for trace and ultra-trace Hg analysis and speciation analysis. This makes routine Hg
458 studies and monitoring impractical in challenging environments such as remote locations or lower-
459 and middle-income countries. Current literature on preserving Hg species in water samples has shown
460 minimal developments on limiting the use of hazardous materials, instead highlighting the need for
461 rapid transportation to a laboratory for preservation. In remote areas and uncontrolled environments,
462 the use of concentrated acids can pose a significant risk to the operator and increase the challenges
463 of transporting samples to laboratories in a timely manner.

464 Solid-phases methods and sorbents are already used in Hg analysis for preconcentration, removal, and
465 speciation of Hg, immobilising the chemical species without altering the chemical forms. Mercury-
466 specific functionalized sorbents, in particular functionalisation with diethyldithiocarbamate or
467 diphenylthiocarbazone, have shown effective extraction of Hg^{2+} and some organic Hg species from
468 natural water samples and suitable recovery after 1 week of storage. There is a lack of literature on
469 the concentrations of adsorbed Hg species after 1-week of storage, therefore research into the long-
470 term storage of Hg-species, particularly MeHg, is necessary for the development of SPE as a
471 preservation method. However, SPE is a relatively inexpensive and safe method for *in-situ* sampling
472 and preserving Hg species from natural water samples for transport from field-to-laboratory and
473 obtaining representative dissolved Hg data.

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