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Sampling and Analysis for Mercury in Steam Collected from Geothermal Wells and Fumaroles

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ABSTRACT

Elemental mercury (Hg^0) is the predominant form of mercury found in chemical surveys of wells at New Zealand's geothermal fields. Mercury is an environmental pollutant and in New Zealand, resource consents limit the discharge to atmosphere. Unacceptable variation in analyzed "total" mercury in steam within duplicate samples and between sampling rounds at various geothermal fields has led to a reassessment of the sampling methodologies. However the cause of the problems was poorly understood. It was thought the variability was due primarily to sampling artifacts caused by the high volatility of Hg^0 or perhaps to an inadequate sample preservation and digestion prior to analysis.

In this study we evaluate the effect of sampling methodology (sampling vessels) and preservative (permanganate and dichromate) and digestion procedures used on the final result. It appears that sampling methodology has the greatest effect on the variability observed.

The direct collection of steam into evacuated glass ampoules containing acid dichromate preservative with no subsequent hot digestion is the most convenient and simplest procedure for obtaining good analytical agreement between replicates. Samples collected using acid permanganate preservative, which is a stronger oxidizing agent than acid dichromate, with or without hot digestion prior to analysis, also gave comparable results. In this situation dichromate appears to be as equally effective as permanganate for converting Hg^0 to a fixed but reducible form. The exception is in the presence of native sulphur,

Ampoule sizes can be increased to accommodate high NCG which would otherwise limit the sample size. Alternatively, where a sufficiently large sample cannot be conveniently collected into an evacuated ampoule, the steam/gas can be passed (natural over-pressure or a pump on the outlet) through a two flask train containing dichromate preservative. This can also give comparable results to samples collected in ampoules but requires much greater care in sample collection.

It is recommended that careful evaluation of sampling and analysis methodologies for mercury in steam, best suited to the steam composition under study, be undertaken prior to the commencement of an ongoing routine sampling and analysis programme. This will save time, effort and may also considerably reduce expensive analytical costs.

1. INTRODUCTION

The ubiquitous presence of Hg in hydrothermal environments and the concern due to the bioaccumulation of mercury in the environment has resulted in numerous studies on the occurrence and behaviour of Hg in geothermal areas (Christenson and Mroczek, 2003; and references therein).

Steam and gas discharged from geothermal power stations contain trace amounts of mercury and considerable effort is being expended internationally to develop technologies for mercury removal in both geothermal and coal-fired power plants (e.g.Vitolo and Pini, 1999; Vitolo and Seggiani, 2002; Peltier, 2003; Schofield, 2004).

Previous studies by Robertson et al., (1977, 1978) and backed up by experience in New Zealand (Christenson and Mroczek, 2003) show that essentially all the mercury in geothermal steam and gases is Hg^0 which is unreactive, even at high H_2S levels. Hg^0 also has a high vapour pressure and is consequently highly volatile. This means that in New Zealand geothermal power stations with direct contact or binary condensers most of the mercury leaves via the power station cooling towers and offgases. The exception is at Wairakei with its complex arrangement of condensers and coolers (Timperley and Hill, 1997). Modeling showed that the estimate of mercury discharged to the river in the condensate could be accounted for by assuming an equilibrium distribution of Hg^0 between vapour and liquid in all parts of the Wairakei power station (Taylor et al., 2001). Hence Operators undertake regular monitoring of mercury in the incoming steam to estimate emissions to the atmosphere.

Prior to the commencement of regular monitoring at one power station, duplicate test samples were collected on the same day and also on the different days (Glover Pers. Comm., 2000). Total steam mercury varied considerably between the samples, the worst difference was when duplicate samples gave 94 and 15 µg/l of condensed steam. This was of great concern given that power stations in New Zealand have to observe mercury discharge limits as part of their operational consent.

Based on this test, the results of Timperley and Hill (1997) and unpublished work of Timperley at the Wairakei Power Station, Glover (Pers. Comm., 2000) conjectured that:

- acid permanganate seems to be the more reliable reagent to use as a preservative since acid dichromate may not oxidize all the Hg^0
- bubbling through acid permanganate as a collection technique would be better than through acid dichromate as less Hg would be lost.
- collection into acid permanganate in a closed ampoule will ensure no Hg is lost during collection.
- hot digestion prior to analysis is necessary

The sampling procedure was subsequently modified which successfully improved the repeatability and reproducibility of the total mercury in steam analyses. However it is not clear whether the adopted procedure, discussed below, is the simplest yet most reliable method of collecting and analyzing Hg in geothermal steam or whether it is preferable to use a closed ampoule or a bubble through method of sample collection.

In this study we evaluate the effect of sampling methodology (ampoules or flasks), the use of preservative (permanganate and dichromate) and digestion procedures on the final result.

2. REFERENCE METHOD FOR MERCURY

Analytical methods applicable for analyzing mercury in steam are based on the reference methods APHA 3112B (Clesceri et al., 1998) and EPA Method 245.1 (EPA 1982). Both are very similar and comprehensively describe the instrumental analytical procedures for analysing total mercury by cold vapour atomic absorption.

In the reference method, an aliquot of a water sample is transferred to a BOD bottle or equivalent closed-system container. The sample is digested with a dilute potassium permanganate-potassium persulfate-nitric acid solution for two hours at 95 ^{o}C. The digestion oxidizes all forms of mercury to Hg(II). The Hg(II) in the digested water sample is reduced with stannous chloride to elemental mercury which is sparged from the sample and detected by atomic absorption to a reporting limit of 0.2 µg/l. The measurement step is now usually performed using an automated mercury analyser, which avoids the analysis of the entire digested sample.

3. STANDARD OPERATING PROCEDURE FOR COLLECTION OF STEAM SAMPLES FOR MERCURY

After the initial problems were identified, the following procedure for collecting geothermal steam for mercury was adopted. A steam sample is collected (via a T piece venting to atmosphere to reduce pressure) and condensed into an evacuated ampoule with a Teflon stopcock (volume ~350 cc) containing 10 ml of concentrated sulphuric acid. At the laboratory 10 ml of 4% potassium permanganate is subsequently added to the ampoule. The ampoule is then shipped to our contracting laboratory which analyses the samples by automated cold vapour absorption spectrometry following a modified method based on reference method APHA 3112B. The contracting laboratory adds additional potassium permanganate if required, extracts the whole sample from the ampoule and 20 ml is digested prior to analysis (J. Watson, Pers. Comm., 2003).

For this study all samples were analyzed in-house using methods adapted from the above reference methods.

4. SAMPLING STEAM FOR MERCURY

Good results require competent sampling techniques. Vigor-Brown and Timperley (1981) recognized that much of the error present in mercury analysis is due to contamination and loss of mercury during sample collection and analysis. All equipment past the stainless steel Webre or main pipeline fitting must be cleaned. Glassware and inert Teflon fittings are conveniently cleaned with chromic acid. This reagent is easily prepared by adding 1**l** of concentrated sulphuric acid to 35 ml of saturated sodium dichromate solution (250 g/100 ml water). The glassware is rinsed/soaked in cold chromic acid for a minimum of one hour but is often left soaking overnight. Protective clothing and eye protection must be worn when using chromic acid. Vigor-Brown and Timperley (1981) also noted that mercury is condensed to metallic mercury when steam is condensed in tubing to the sampling flask. This leads to particulate mercury entering the sampling flask which is likely to limit reproducibility. To minimize this possibility, an insulated Teflon hose (with a stainless steel over-braid) is used to transport the hot steam (after the T piece) to the sampling flask without condensation. The hose is cleaned by filling with 10% v/v of nitric acid as are other fittings unable to be cleaned in chromic acid. Butyl rubber hoses, normally used to sample steam, are a source of mercury contamination and are difficult to clean.

Two types of sampling bottles were used in this study, a ~ 350 cc glass ampoule (Giggenbach, 1975) and two 150 ml Erlenmeyer flasks in series with B24 ground glass joints each fitted with a Dreschel head with a stem length sufficient to place the coarse sinter just off the bottom of the flask. Teflon clips keep the heads firmly in place (as well as stoppers, air condensers etc) and the flasks are connected with a short piece of silicone tubing.

Steam enters the evacuated glass ampoule and is condensed by cooling the outer surface, usually by a stream of cool water or dunking in a bucket of water. Non-condensable gases limit the amount of condensed steam that can be collected in this manner, typically 10 – 20 ml depending on NCG, but the volume of the ampoule may be increased to compensate. For example, at a high gas field such as Ngawha (average 18 wt % CO_2 in steam), a 2 l ampoule, with Teflon stopcock at either end, is used to sample for mercury in steam. Ampoules of this size are expensive, difficult to handle, clean and transport in the field.

In contrast to the ampoule, the flask train is placed in a shallow tray of ice water mixture and steam is collected at a slow rate, typically 1-2 ml of condensate per minute to a total volume between 20 and 30 ml in the first flask. The weight change in the second flask is negligible. The overpressure is adjusted until gas appears to “effervesce” at the sinter in the first as well as the second flask.

When collecting the sample it is important to ensure that all condensate at the neck of the ampoule is transferred as this will lead to errors in estimating the mercury concentration in steam, particularly at small sample volumes; similar attention needs to be paid when passing steam through the flasks. Subsequent addition of reagent to the ampoules is facilitated if the samples are not collected to “completion”. This ensures a very slight negative pressure after collection.

In this study two different wells were sampled using a webre separator as well as one natural fumarole. The fumarole was sampled by inserting titanium tubes in the active vent and condensing steam into an evacuated ampoule or sucking steam through a flask train using a small diaphragm air pump at the outlet.

The well and fumarole steam did not contain any oxygen.

5. ANALYSIS

5.1 Introduction

The high volatility of Hg^0 requires the condensed steam/gas sample to be either collected into a closed vessel or directly into an “open” vessel containing an oxidizing preservative. Subsequently preservative is also added to the closed vessel, in our case a glass ampoule, if this was not initially present. It is assumed that the preservative efficiently fixes

Hg^0 to non-volatile Hg(II). The complication is that geothermal gas streams may contain appreciable quantities of H_2S gas which reacts with the oxidizing preservative. This side reaction may compete and inhibit the efficient oxidation of Hg^0, particularly when bubbling through a progressively reducing concentration of preservative. Also, the NCG could purge and drive the Hg^0 out without oxidation.

5.2 Preservatives

Two reagents are commonly used as oxidizing agents: acid permanganate as in the reference method above and acid dichromate. Collecting samples into acid permanganate has its drawbacks. This reagent is unstable (manganese dioxide, MnO_2, begins to precipitate) almost certainly reducing the oxidizing efficacy over a day of sampling. Diluting the reagent to minimize the decomposition is not an option for use in ampoules as this reduces the sample volume that can be collected. Similarly in flasks, the concentration needs to be higher rather than lower to ensure that all the Hg^0, in a stream of H_2S, is fixed. Minimizing reagent volume and maximizing sample volume also increases the detection limit and accuracy. Adding permanganate to ampoules containing acidified condensate after sample collection, which is the currently accepted standard operating procedure used in our laboratory, avoids the prior degradation of the preservative. MnO_2 still precipitates but this also occurs during collection of steam directly into acid permanganate. The presence of the MnO_2 precipitate means that the sample cannot be effectively sub-sampled. As a consequence the method of Standard Addition to verify analytical accuracy cannot be readily used. Standard addition of a known quantity of mercury, after the precipitate has been reduced to Mn^{2+} by hydroxylammonium chloride but prior to analysis, may give a false confidence in the quantity of mercury recovered; i.e. the addition may be recovered but not the whole portion of the geothermal mercury.

In contrast acid dichromate is an “easier” reagent to use. It is stable, no precipitate forms (with one important proviso discussed below) and blanks for the relatively inexpensive analytical grade potassium chromate (addition of acid results in dichromate formation) are typically as low as for the considerably more expensive “low mercury” grade potassium permanganate. However of the two, acid dichromate is a weaker oxidizing. This solution turns from bright orange to brown as the dichromate is progressively reduced to Cr^{3+} and finally to green when it is completely consumed.

5.3 Sample Collection and Analysis Treatments

Table 1 lists the typical concentrations and volumes of reagents used in the ampoules and flasks. These were determined by trial and error so that after sample collection the solutions in the flasks were still either pink if permanganate was used or brown if dichromate was used. Figures 1 and 2 show the various sample treatments.

5.4 Reagents

The potassium permanganate, stannous chloride and hydroxylammonium chloride were all BDH “SpectrosoL” grade; the 1000 mg/l mercury standard was Merck “CertiPUR” and the concentrated hydrochloric acid was BDH “Aristar” grade. All other chemicals used were BDH “Analar” grade. The sulphuric acid (conc.) was used only if the mercury content was less than 0.2 µg/l while the nitric acid (conc.) was distilled before use, either in a quartz or sub-boiling in Teflon bottles. Working 50 and 100 µg/l mercury standards were prepared daily from a 2.5 mg/l stock (0.5% wt/v potassium chromate & 0.5% v/v sulphuric acid).

All solutions were simply made up with tap water which is low in mercury (~6 ng/l) at about the same level as the laboratory distilled-deionized water. The mercury in the distilled water is likely to be from air borne contamination from nearby geothermal power stations. This is of no consequence as the tap water has mercury content over 1000x lower than the steam sample concentrations.

Table 1. Preservative Solution Volumes

Treatment	volume (ml)	
	Ampoule	**Flask**
A		
10 wt% potassium chromate	10	10
Water	25	50
sulphuric acid (conc.)	10	10
B		
5 wt% potassium permanganate	15	15
Water	25	50
sulphuric acid (conc.)	10	10
C		
sulphuric acid (conc.)	10	-
C1 5% potassium permanganate added after sample collection	15	
OR		
C2 10% potassium chromate added after sample collection	10	-

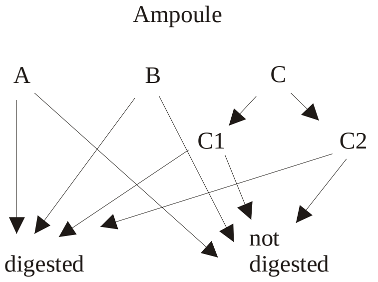

Figure 1: Ampoule collection and analysis treatments

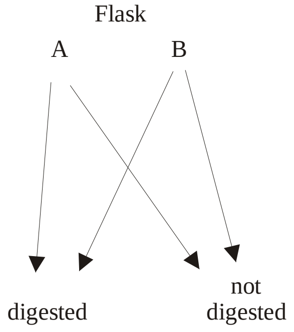

Figure 2: Flask collection and analysis treatments

5.5 Sample Processing

Samples were processed both immediately and up to 1 week after collection and were either digested or not digested. The amount of sample collected was determined by weight difference, assuming the density of water. If necessary, water was added to bring all the sample weights up to a common value. Thus if sample weights for a batch fell between 20 and 25 g all samples were diluted to 25 g. Standards were then made up in the same proportion (sample and reagents) as the samples. This procedure was followed to avoid matrix effects (see section 5.6).

If permanganate preserved samples were to be digested, an additional 5 ml nitric acid (conc.) and 8 ml 5 wt% potassium peroxodisulphate were added followed by heating on a water bath for 2 hr at 95°C (following EPA method 245.1). If dichromate was the preservative, the samples were simply heated to 95°C for 2 hours. Usually no additional dichromate was added as it never appeared that all the dichromate had been consumed during sample collection. Samples were digested in-situ in the collection vessels. The 150 ml collection flasks were fitted with 300 mm air condensers (stoppered with glass balls to avoid sticking) while for the ampoules the Teflon stoppers were cracked open before placement in the water bath.

5.6 Analysis

The samples were analyzed using an automated Perkin Elmer FIMS 100 Mercury Analysis System using 1.1 wt% stannous chloride in 3 % v/v hydrochloric acid as reductant and 3% v/v hydrochloric as the carrier solution. To achieve good results with the flow through technique it is very important to appreciate that the kinetics of reduction of the Hg(II) appears to be greatly affected by the sample matrix (e.g. acidity, quantity of hydroxylammonium chloride and so on). This means that the standards must be processed in exactly the same manner as the samples to achieve quality results.

The quality assurance of the analyses was maintained by analyzing with the every sample batch a certified sample diluted from the NIST “Standard Reference Material” 1641d Mercury in Water (1.590 mg/l). Typically the NIST standard agreed within 7% of the certified value but at these concentration levels agreement within 10% was considered acceptable. The certified sample was processed exactly in the same manner as the samples and standards.

Prior to analysis 6 ml of 12 wt% sodium chloride- 12 wt % hydroxylamine hydrochloride was added to all samples, whether digested or not, to remove excess preservative.

Selected batches were reanalyzed between 1 and 3 weeks after the initial analysis.

6. RESULTS

In Table 2, are listed the steam mercury concentrations of samples which were collected and analyzed according to the treatments outlined in Table 1 and Figures 2 and 3. The quality of the results increased and the variability decreased with time as the techniques were developed and the preservative solutions optimized. The table also shows the certified sample concentrations (viz. the mercury reference standard diluted to the right range expected for the samples) as well as the results of one composited sample which was spiked in the method of standard additions. What is not shown in the table is the lack of difference between digested and non digested samples, either in ampoules or flasks, with respect to the time interval before initial processing and also that there was no apparent loss of mercury on reanalysis one to three weeks later.

In earlier runs the samples were diluted with water to 100 ml (excluding reagents). In the flasks, considerably more reagent volume (at times up to 100 ml) was used than in the final “optimized” volumes shown in Table 1. This had the effect of diluting the samples up to 10 x (sample plus reagents) with consequent loss of precision. Overall good consistency was achieved in a series of duplicate samples. However there were always samples with higher or lower mercury content than the average for the batch. In this regard the use of the mercury reference standard is critical as it confirms the reliability of the analysis. In these runs the reference standard, diluted and processed in the same manner as the steam samples, was typically within 7% of the certified value. This immediately gives confidence in the analytical method and also confirms that the variability is almost certainly due to the sampling artifacts. These are either in sampling technique or may be due to unstable or variable well composition (Christenson and Mroczek, 2003). A “synthetic” mercury QA sample was also analyzed with every batch however to date insufficient values have been collected to confirm the stability of the QA sample.

Conclusions that may be drawn from the data are the following:

a) For collection into an ampoule it makes no difference if the permanganate is present prior or added after the collection (**Run 6**).

b) In contrast there is a large difference between adding chromate before or after. In **Run 2b** and **3b** native sulphur was formed after adding acid dichromate or 10% chromate to acidified condensate. Interestingly, reheating the former resulted in recovery of portion of the mercury. However, this was not the case in the latter situation. This was not investigated further.

c) Collecting condensate into acid dichromate, either ampoules or flasks, does not result in the formation of native sulphur (**Runs 3c, 3d, 4b, 5, 7b**).

d) There was no significant difference between the permanganate digested and non digested samples, either in flasks or ampoules. (**Runs 6, 7a**)

e) Similarly for dichromate (exceptions were noted in (b) above) (**Runs 3c, 4b, 5a, 7b**)

f) Overall the data suggests that steam collected into flasks or ampoules are comparable, using either reagent, digested or not.

The last point requires further clarification. In **Run 3a** where the permanganate was added to the ampoule after the collection, the analyzed mercury appears distinctly higher than in the other samples in the **3** series (ignoring 3b). However, agreement between treatments is observed for **Runs 1** and **4**, and **Runs 5a** and **6c, 6d**. Similarly dichromate flask **2d** appears higher than for the remaining **2** series samples, but again the results for dichromate **Run 3e** are comparable to **3c** and **3d**. That the results are not

Table 2. Steam mercury concentrations (all µg/l).

Run	Treatment	Vessel	i	ii	iii	iv	v	vi	vii	Average	SD
1a	C1	Ampoule	20.5	22.4	21.2					21.4	1.0
1b	A†	Ampoule	20.3	27.1	27.4	23.7	19.8			23.6	3.6
2a	C1	Ampoule	20.2	15.5	17.0	17.1				17.4	2.0
2b	C2	Ampoule	16.4	18.3	15.4	10.2	8.6	10.5			
2c	A *	Flask	19.7	20.0	20.6					20.1	0.5
2d	B **	Flask	25.7	24.0	22.4					24.0	1.7
3a	C1	Ampoule	21.2	21.5	19.6	19.8				20.5	1.0
3b	C2	Ampoule	3.1	2.5	4.7	4.7					
3c	A***	Ampoule	16.8	16.2	16.4	16.8	16.6	18.0	17.5	16.9	0.6
3d	A *	Flask	17.6	17.9	17.2					17.6	0.4
3e	B **	Flask	18.8	16.5	18.9					18.1	1.4
	Certified - permanganate		13.6	12.7	6.5%						
	Certified - dichromate		6.7	6.4	5.1%						
4a	C1	Ampoule	21.0	22.1	21.9	22.1	19.8	22.0	22.9	21.7	1.0
4b	A	Ampoule	23.5	21.9	22.5	26.4	22.6	22.8	22.0	23.1	1.6
	Certified - permanganate		9.08	8.5	6.1%						
	Certified - dichromate		13.6	12.7	6.5%						
5aΔ	A	Ampoule	45.9	39.1	39.4	39.0	40.5	37.4	40.9	40.3	2.7
5b‡	A	Flask	16.5	10.3	9.5					12.1	3.8
	Certified - dichromate		25.4	23.9	5.9%						
6a	C1	Ampoule	20.4	21.1	19.5	20.0				20.3	0.7
6b	B	Ampoule	18.4	21.7	22.1	20.1				20.6	1.7
6cΔ	C1	Ampoule	37.9	36.2	38.1	38.4				37.7	1.0
6dΔ	B	Ampoule	34.3	36.8	38.1	39.1				37.1	2.1
	Certified - permanganate		12.5	11.3	9.6%						
7a	B	Flask	17.0	14.5	16.8	16.6				16.2	1.2
	Certified - permanganate		13.3	12.7	4.4%						
7b	A	Ampoule (7 composited)	concentrations are µg/l in **total** – sample plus reagents.								
			Measured	Actual	% difference						
	Certified - dichromate		2.0	2.1	3.8%						
	digested		3.5								
	1x spike digested		5.5	5.3	2.3%						
	2x spike digested		6.3	6.2	1.4%						
	No digestion		3.5								
	1x spike no digestion		5.4	5.2	4.6%						
	2x spike no digestion		6.4	6.1	5.2%						

* 100 ml acid dichromate soln., ** 75 ml permanganate soln., *** 35 ml acid dichromate, † Extra fresh dichromate solution added for digestion, ‡ Alternate well, Δ Fumarole

No Digestion

Measured Actual % Difference

consistently in one direction suggests that the differences are not due to one of methods trapping more of mercury than the other. The earlier results (**Runs 1-3**) were also undertaken when the sampling and analysis methodologies were being developed.

In flasks, the possibility was raised that if the kinetics of the mercury oxidation by the preservative is slow then not all the mercury would be trapped. Using dichromate preservative, carryover of mercury to the second flask was typically less than 10% of the total while with permanganate preservative the carryover was typically halved. Loss from the second flask is likely to be less as a proportion as preservative strength is maintained throughout the collection period. This means that a two flask train is adequate to trap a minimum of 99% of the total mercury, the remainder of which is less than the subsequent uncertainly in the analysis.

The efficiency of the preservative is dependent on the amount of H_2S in steam. For purposes of comparison the separated well steam NCG was ~ 2 wt% in total of which ~ 0.08 wt% was H_2S. In comparison the Rotokawa fumarole NCG is typically ~ 5 wt% of which ~ 0.1 wt% is H_2S.

7. DISCUSSION

The standard operating procedure for mercury sampling in this laboratory was developed from work undertaken by Timperley and Hill (1997) in their study of mercury in the Wairakei power station of river's water condensates. They found that both un-preserved and preserved (irrespective of the preservative used) samples left for more than a few hours lost their stannous chloride reactive mercury (and to a lesser extent also sodium borohydride). After about 24 hr no mercury could be recovered by the addition of stannous chloride. If samples were spiked and then left, the spike also became non-recoverable. If the samples were spiked and analyzed immediately, the entire spike was recovered. This would give a false impression that all is well. They found that the only way to convert the lost Hg back to a form that can be recovered by stannous chloride is to hot digest the samples with the acid preservative, either acid dichromate or acid permanganate, boiling for about 60 minutes in flasks fitted with air condensers with additional preservative added if required.

They speculated that the cause for this behaviour was the formation of HgS which cannot be readily reduced by stannous chloride and only slowly dissolves in acid solution (Timperley and Hill, 1997).

In subsequent work undertaken by Timperley at the power station (as reported by Glover, Pers. Comm. 2000) the mercury in the offgases, which also contains appreciable quantities exsolved oxygen from the river water, was underestimated. The explanation for the low results was that the acid dichromate did not oxidise all the elemental Hg in the sampling flask so that when the sample was drained from the sampling flask to the digestion flask some was lost into the atmosphere. Subsequent sampling into acid permanganate showed that no Hg^0 was present in the sample flasks at the stage when the samples were transferred to the digestion flasks.

The condensates Timperley and Hill (1997) were analyzing were aerated river water containing small amounts of H_2S and trace amounts of mercury < 150 ng/l. These fluids are vastly different to the well and fumarole steam condensates collected and analyzed in this study. In particular, mercury in steam is elemental at over 1000x the concentration and contains no oxygen. The Wairakei offgases containing oxygen are again quite different from flashed steam. During collection it is possible the oxidation of H_2S formed a small amount of sulphur which is a known effective scavenger for mercury (Christenson et al., 2002).

As shown in this work the sulphur formed when acid dichromate or chromate was added to acidified condensate very effectively scavenged Hg(II) to a form which was non-reducible without a digestion step. In contrast adding permanganate to acid condensate results in oxidation of Hg^0 to dissolved Hg(II) and H_2S to sulphate without the formation of sulphur, or at least any sulphur initially formed is oxidized through to sulphate.

8. CONCLUSIONS

It appears that for geothermal steam containing no oxygen the sampling can be undertaken either using flasks or ampoules, with either acid dichromate or acid permanganate and without the necessity for a digestion step prior to analysis.

1. The best and easiest method is to collect the steam into evacuated glass ampoules. Collection into flasks is more involved and time consuming but perfectly feasible if a larger sample needs to be collected or if the NCG content is high. The latter, of course, doubles the analyses per sample.

2. Acid permanganate slowly decomposes so when collecting a sample into an evacuated ampoule it is preferable to add permanganate to the acidified condensate after sample collection. Sufficient permanganate must be added to ensure that all of the H_2S is oxidized. Acid permanganate for use in flasks suffers from the same drawbacks but at the concentrations suggested in this study can be made daily and should be used within 8 hours.

3. Acid permanganate is a stronger oxidizing agent than acid dichromate However if the steam contains only Hg^0 and no oxygen (based on Timperley and Hill's (1997) study), the sample may be collected by condensation into a flask or evacuated ampoule containing acid dichromate. Adding acid dichromate to acidified condensate in an ampoule after sample collection results in sulphur formation which fixes the mercury to a non-reducible form. It is easier to use acid dichromate with flasks, especially if there is a time delay before sampling.

4. Before embarking on a mercury monitoring programme the sampling methods and analyses need to be thoroughly tested. The avoidance of a digestion step, especially when using acid permanganate, would greatly simplify and speed up the analytical procedure.

5. The use of certified standards and QA samples to avoid analytical problems is mandatory since it is difficult to collect a “perfect” set of replicate samples and it is important to quantify sampling errors.

6. If using an automated flow system it is important to take into account matrix effects. This means that all samples and standards have to be processed in the same consistent manner.

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