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MASS FLOW MEASUREMENT BY ALCOHOL TRACER DILUTION

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ABSTRACT

Field trials have shown that isopropanol and butan-2-ol can be used for the accurate measurement of steam flow in two-phase pipelines. These steam phase tracers are injected as liquids using conventional metering pumps and sampled quantitatively at downstream sampling points by collection of steam condensate and brine into simple screw-cap bottles. Composite steam-liquid tracers can be prepared by mixing isopropanol and a water phase tracer (e.g: benzoate or rhodamine WT).

Alcohols can be analysed to a high accuracy and at relatively low cost by established procedures developed for blood-alcohol analysis. Only small samples are required (<10 mL) and these can be air-mailed to laboratories at low cost. The use of alcohol tracers allows significant simplifications to be made to tracer dilution equipment and procedures, with a resulting reduction in overall costs.

1. INTRODUCTION

Chemical tracers have been used since the early 1990's for measuring mass flow in pipelines. This has included magnesium tracers for brine flow measurement (Macambac *et al.*, 1998) and, more recently, dual tracer methods for measurement of flows in two-phase pipelines (Hirtz *et al.*, 1993; Hirtz and Lovekin, 1995).

Tracer dilution mass flow measurement has the major advantage of allowing production wells to be tested while in service, reducing the need for expensive testing plant and discharges of fluid to the environment. With environmental constraints becoming more stringent, it is inevitable that on-line testing will become more important.

This paper presents the results of tracer dilution development work carried out for Tuaropaki Power Company, who are evaluating the tracer dilution method for use at the recently commissioned Mokai power station in New Zealand. The field work was carried out at the nearby Rotokawa power station which has very similar operating conditions.

1.1 The Tracer Dilution Method

The principle of two-phase mass flow measurement by tracer dilution is described in detail by Hirtz *et al.* (1993). Separate water and steam phase tracers are injected into the two-phase pipeline at a known rate. At downstream sampling points, separated steam and water samples are collected which have tracer concentrations that are directly dependent on the flow (the higher the flow the lower the tracer concentration). The expression for calculating steam flow (SF), where the steam tracer is entirely in the steam phase is:

$$\text{SF (t/h)} = \frac{\text{tracer injection rate (g/h)}}{\text{tracer conc in steam (g/t)}} \qquad \text{- (1)}$$

The calculation for water flow is analogous and from the measured steam and water flows (SF, WF), the total discharge enthalpy (Ht) can be calculated:

$$\text{Ht} = \frac{\text{SF hg} + \text{WF hf}}{\text{SF} + \text{WF}}, \qquad \text{- (2)}$$

where hg and hf are the known enthalpy of steam and water at the pipeline temperature (obtained from steam tables).

Currently available tracer dilution procedures use compressed gas for the steam phase tracer (SF_6 is favoured) and salt solutions such as sodium benzoate for the water phase (e.g: Macambac *et al.* 1998). Although well proven, the equipment and analytical costs are high. In an effort to develop simpler, less expensive methods, Lovelock (1997) investigated using low boiling point organic liquids rather than compressed gases as steam phase tracers. Such compounds are gaseous at pipeline temperatures and pressures but can be injected as liquids using the same dosing pumps used for liquid-phase tracers. This allows major simplifications to be made to injection equipment and sampling procedures, as only liquids are being handled. Initial field trials showed that isopropanol / bromide tracers gave steam flows close to those measured by the James lip-pressure method (James, 1970).

The field trials described in this paper are an extension of the work of Lovelock (1997), and were undertaken for the purpose of rigorously evaluating the accuracy of alcohol tracers.

2. ORGANIC LIQUID TRACERS

Table 1 lists a number of commonly available, low-boiling point, organic liquids which have potential as steam phase tracers. These compounds can be divided into two groups: (1) the less soluble, "purgable" organics (e.g: chloroform, hexane, benzene) and (2) the soluble organics (e.g: alcohols).

The first group can be expected to perform well as vapour tracers and, because of their low solubility in water, will exist almost entirely in the steam phase. However, they may require special procedures for quantitative sampling. If steam is simply condensed and collected into open containers, there is potential for the volatile organics to be purged as noncondensible gases are exsolved (particularly if the gas content of the fluid is high). To prevent this, the tracers may need to be collected into evacuated gas flasks or absorbed into organic solvents. This reduces their advantages over compressed gas tracers. Also, the analysis of these volatile organics (typically by trace-level GC-MS) is expensive. Lovelock (1997) had limited success with chloroform tracers in low-gas discharges, but a single test of chloroform in this study produced only low concentrations in steam condensate indicating loss of the tracer with exsolved gas.

Adams (1995) discussed the potential application of alcohols in reservoir tracer tests, and recognised their potential as two-phase reservoir tracers, (i.e: tracers that would be distributed between reservoir steam and water phases). However, alcohols have some drawbacks as reservoir tracers: established analytical methods are not sensitive enough for the low levels seen in returning fluid and some alcohols (e.g: isopropanol) decay within the period of tracer tests. Neither of these problems apply to pipeline mass flow dilution tests where residence times are in the order of seconds, rather than days, and concentrations can be orders of magnitude higher. Also, the fact that alcohol degrade at high temperature means there is no long-term contamination of the reservoir by injected fluids.

It is possible that alcohols have not been pursued as mass flow dilution tracer because of the solubility of alcohol gas in water, e.g: at 190°C the steam-water distribution of isopropanol gas is about 16:1 (Lovelock, 1997). This is not a major limitation because a simple correction can be made by analysis of alcohol in the brine:

$$\mathrm{SF\ (t/h)} = \frac{\mathrm{injection\ rate\ (g/h)} - [\mathrm{WF\ (t/h)} \times T_W\ \mathrm{(g/t)}]}{T_S\ \mathrm{(g/t)}} \qquad - (3)$$

where TW and TS are the alcohol tracer concentrations in water and steam and SF and WF are the steam and water flows. The correction is relatively small for medium to high enthalpy discharges and so the water phase alcohol concentration does not need to be known to the same accuracy as the steam phase concentration. The concentration of gas tracer dissolved in water can either be measured directly or calculated using an assumed distribution ratio. The water flow must also be known, which would be the case if an independent water-phase tracer is being used.

The major advantage of alcohol over all other steam phase tracers is that sampling is so much easier. Because the alcohols are polar, they are not easily purged by exsolved noncondensible gas. Past results (Lovelock, 1997) suggest that alcohol can be sampled quantitatively by simple condensation of steam through a cooling coil and collection into screw-cap glass containers.

Of all the readily available alcohols, isopropanol and butan-2-ol are considered to be most suitable. Less attractive is ethanol which has a relatively lower steam/water distribution ratio (Lovelock, 1997). Butan-2-ol has a boiling point very close to that of water (99.5°C) but at higher temperatures has a vapour pressure well above that of water. Accordingly, it can be expected to be gaseous in saturated steam-water mixtures throughout the temperature range found in two-pipelines. Isopropanol has the advantage of being miscible in aqueous solutions and can be used to prepare composite steam/water tracers, for example with benzoate. This would not be so simple with butan-2-ol, which has a solubility of 12.5% in water (Table 1). Isopropanol is an inexpensive chemical (about US$4 per litre in New Zealand for 99.5% grade) while butan-2-ol is 2-3 times the cost.

3. METHOD

3.1 Equipment and Procedures

The tracer dilution tests for this study were carried out at the Rotokawa field in New Zealand, which currently has a 24 MWe power plant supplied by two production wells (RK5 and RK9). The field is a high-temperature (330°C max), liquid-dominated resource with low salinity (2000 mg/kg TDS) and a gas content of 0.5 - 1%.

The tracer tests were carried out on the two-phase lines of the two production wells, which have very similar output characteristics (as confirmed by the results of this study). The pressure throughout the two-phase line and at the production separator is 20-25 b.g. (215 - 225°C). This is near he upper limit for operating conditions in conventional geothermal developments. Downstream of the production separator, water and steam flow are logged by orifice plate and annubar respectively. These flows were used to assess the accuracy of the tracer dilution measurements, in this study.

Figure 1 shows the layout of the tracer injection rig fabricated for the field trials. This includes a double-head Bran & Luebbe metering pump, rated to 80 bars and with a high stroke rate (144 strokes/min). Injection was carried out close to the wellhead though ¼" tubes inserted through existing sampling points. No pulsation damping was used. The mean dose rates over the period of each test were measured by weight loss from a header tank. Samples of separated steam and water were collected downstream using an insulated webre sampling separator operating at the pipeline pressure. The separated steam and water were condensed and cooled to near ambient temperature through coiling coils and samples were collected over a 1-2 minute period to average out variations due to pump pulsation or accumulation of tracer within the injection port. Tracer-dilution runs typically lasted 10 - 20 minutes.

3.2 Minimising Errors

Mass flow dilution measurements involve many steps and have the potential to have high cumulative errors. A number of things can be done to minimise these errors, the key one being the preparation of laboratory calibration standards from the actual tracer solutions used in the field. This effectively cancels out any errors associated with preparation of the stock solution (i.e: the denominator and numerator in equation (1) change by the same degree).

To minimise matrix effects in the analytical process, calibration standards can be prepared in brine matching that of the samples being collected. To reduce the number of measurements in the field, composite tracers can be used (see 4.2 below).

3.3 Alcohol Analyses

The alcohol analyses performed for this study were carried out by the ESR Alcohol Analysis Unit in New Zealand, a laboratory whose primary function is the analysis of blood samples for evidential purposes. Methods for the analysis of alcohol in blood are well established and automated and little additional development was necessary to provide high quality analyses of the geothermal samples. Alcohol concentrations in the tracer dilution samples were in the range encountered routinely in blood analyses. Only small sample volumes are required (<10 mL) and samples can therefore be air-mailed quickly and at low cost to laboratories.

For this study 30 mL samples were collected and treated with about 20 mg of zinc acetate (to precipitate H_2S) and 0.3 g of NaF. The H_2S is precipitated primarily to protect the GC column and detector rather than to remove interferences. NaF is used routinely for preserving blood samples for alcohol analysis but is probably not necessary for sterile geothermal samples. The GC detector response is dependent on the partial pressure of alcohol in the head space and this is not affected by the presence of dissolved CO_2 in the samples. The laboratory routinely checks for alcohol degradation products but to date none has been found in the geothermal samples.

The alcohol tracers were analysed by automated head-space gas chromatography. The instrumentation includes a Tekmar 7000 head-space autosampler linked to a Hewlett-Packard 5890 Series II gas chromatograph fitted with a packed column. Data analysis is performed using a Hewlett-Packard 3396 Series II integrator. The detector used is a standard HP flame ionisation detector (FID). FID's are the "industry standard" for blood alcohol analysis by HS-GC and this equipment, or its equivalent, would be commonplace in most laboratories carrying out blood alcohol analyses for evidential purposes.

The gas chromatography column used is a commercially available packed column with the following specifications:

Column material:	Stainless Steel
Length:	6 feet
Outer diam:	one eighth inch
Support:	Graphpac GC
Mesh range:	80/100
Liquid phase:	Carbowax 1500
Liquid loading:	0.2%
Carrier gas:	Nitrogen
Carrier gas flow:	30 mL/min

Columns identical or very similar to this are used for blood alcohol analysis in many countries throughout the world.

All samples and calibrators are diluted 6 fold (0.2 mL sample plus 1.0 mL of internal standard) with the internal standard solution comprising n-propanol and 23 grams of sodium azide per litre. The n-propanol concentration is approximately the same as that of the mid-range calibrator.

Diluted samples and calibrators are sealed within 22 mL headspace vials and incubated for 30 min at 60°C in the autosampler prior to automated injection of 1 mL of the headspace onto the GC column.

Alcohol concentrations are obtained by comparing the alcohol/n-propanol peak area ratios for the samples with those of the calibrators. Calibration curves are always linear over the range of calibration standards used. Because the linearity of the method is very good, it is not normally necessary to construct a calibration curve. Instead, calibration is carried out by multiple dilutions of one of the mid-range standards with a follow-up check of the method by running the other standards as if they were samples. For convenience, blood alcohol analysis software is used to collect and process the raw data generated by the HP integrators.

4. RESULTS

4.1 Isopropanol and Butan-2-ol.

Tracer dilution trials using isopropanol and butan-2-ol were conducted at Rotokawa in June 1999 using the RK9 two-phase line, operating at a pressure of about 21 b.g. On this occasion RK9 was the only well in service so the accuracy of tracer-dilution flowrates could be gauged by direct comparison with power plant steam flows.

The alcohols were injected into the two-phase line approximately 50 m downstream of the wellhead. Sampling was carried out a further 100 m downstream, with two pipeline bends assisting mixing. Residence time in the line, assessed using rhodamine dye, was less than 1 minute. Four separate runs were conducted using alcohol tracers, three using isopropanol (injected at different rates) and one using butan-2-ol. Several samples were collected during each run to assess precision. Results are presented in Table 2.

The alcohol concentrations for each set of samples fall in a very narrow range with less than 0.5% variability for the condensate samples. Calculated steam flows ranged from 120 - 123 t/h for the four tests. This is in good agreement with station annubar measurements of 117 - 120 t/h (mean 119 t/h). The flowrate calculations include a correction for tracer dissolved in the water phase and a mean water flow of 200 t/h (from orifice plate and separate benzoate tracer results) was used for all calculations. The accuracy of the water flow measurement is not critical - in this case a 10 t/h change in water flow gives a 1 t/h change in calculated steam flow.

The steam/water distribution was about 13:1 for the three isopropanol runs and 16:1 for the butan-2-ol. The higher ratio for the butan-2-ol reflects its higher molecular weight and lower solubility in water.

The excellent reproducibility of the alcohol results and the agreement between tracer-calculated steam flows and annubar measurements, confirms that isopropanol and butan-2-ol are attractive steam-phase tracers.

4.2 Composite Steam-Water Tracers

A significant advantage of isopropanol over other organic tracers is that it can be mixed with aqueous water phase tracers to produce a composite water / steam tracer. This reduces the time needed to carry out the tests and allows steam and water flowrate to be measured simultaneously (which may be important if a well is cycling).

For this study a composite tracer comprising 10 wt% benzoate and 40 wt% isopropanol was prepared. Sodium benzoate was chosen because it has already been proven as a water phase tracer by other workers (e.g: Macambac *et al*. 1998). The composite tracer was tested on both the RK5 and RK9 two-phase lines (operating at 24 - 26 b.g.) in August 1999. Results are presented in Table 3.

Calculated steam flows for the first two set of samples (from RK9) fall in a narrow range while for RK5 the steam flow declines slightly during the test. The alcohol concentrations are a little more variable than seen for pure alcohol injection (Table 2) but calculated steam flows are still in a narrow range. The greater variability may be related to the admixture of the aqueous tracer or to the more difficult sampling conditions in this test. Nevertheless, the total steam flow obtained by summing the flows for RK5 and RK9 (141 t/h) is in excellent agreement with the range measured at the station by means of annubars (140-143).

4.3 Rhodamine Tracers

Rhodamine WT, a fluorescent dye compound, has been used as a reservoir tracer (e.g: Rose and Adams, 1994; Bixley *et al.* 1995) and on rare occasions for measuring mass flow (e.g: Osborn and Spielman, 1995). However, there has apparently been little rigorous evaluation of its accuracy for mass flow dilution measurements. Rhodamine has attractive properties as a water phase tracer. As a dye, it provides a visual signal of tracer arrival. It degrades in time in the reservoir and so does not contaminate the system. Analytical instrumentation (fluorometers) is relatively inexpensive compared with that used for chromatographic techniques.

Samples for rhodamine analysis may need to be diluted to avoid precipitation of silica. Experiments conducted as part of this study showed there is significant uptake of rhodamine into precipitated gel and this reduces the concentration in the bulk water (up to 40% in this study).

At high pipeline temperatures (220-230°C for this study) the thermal decay of rhodamine becomes an issue although the decay data of Adams (1995) suggests that at 220°C rhodamine will suffer less than 0.5% decay in 10 minutes. Residence times in pipeline tests will generally be less than one minute.

For this study, rhodamine WT was assessed by combining it with benzoate as a composite tracer (10% benzoate and 0.3% rhodamine), thereby allowing comparison of calculated water flowrates under identical conditions. Rhodamine calculated flowrates fell within in a narrow range for multiple samples (<2%) and were within 5% of flowrates measured by benzoate and orifice plate measurements

5. CONCLUSIONS

Field trials conducted at Rotokawa show that steam flow can be measured to a high accuracy by use of isopropanol or butan-2-ol dilution tracers. Steam flow measurements from 7 separate injection runs are within 1-4% of flows measured independently by annubar.

The use of alcohol tracers, in combination with benzoate or rhodamine tracers, allows major simplifications to be made to tracer-dilution procedures. This in turn has the potential to significantly reduce costs for equipment and manpower.

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Table 1. Selected common organic liquids, potentially suitable as steam phase tracers

Compound	Formula	Formula Weight	Density mg/ml	BP °C	Solubility mg/ml
Hexane	$CH_3(CH_2)_4CH_3$	86.2	0.66	69.0	140
Benzene	C_6H_6	78.1	0.88	80.1	700
Chloroform	$CHCl_3$	119.4	1.49	61.2	8,200
Ethyl Acetate	$CH_3CO_2C_2H_5$	88.1	0.90	77.1	85,000
Butan-2-ol	$CH_3CH(OH)CH_2CH_3$	74.1	0.81	99.5	125,000
Ethanol	CH_3CH_2OH	46.1	0.79	78.4	∞
iso-Propanol	$(CH_3)_2CHOH$	60.1	0.79	82.5	∞
n-Propanol	$CH_3(CH_2)_2OH$	60.1	0.80	97.4	∞
Acetone	CH_3COCH_3	58.1	0.79	56.5	∞

source: Perry and Chilton (1973)

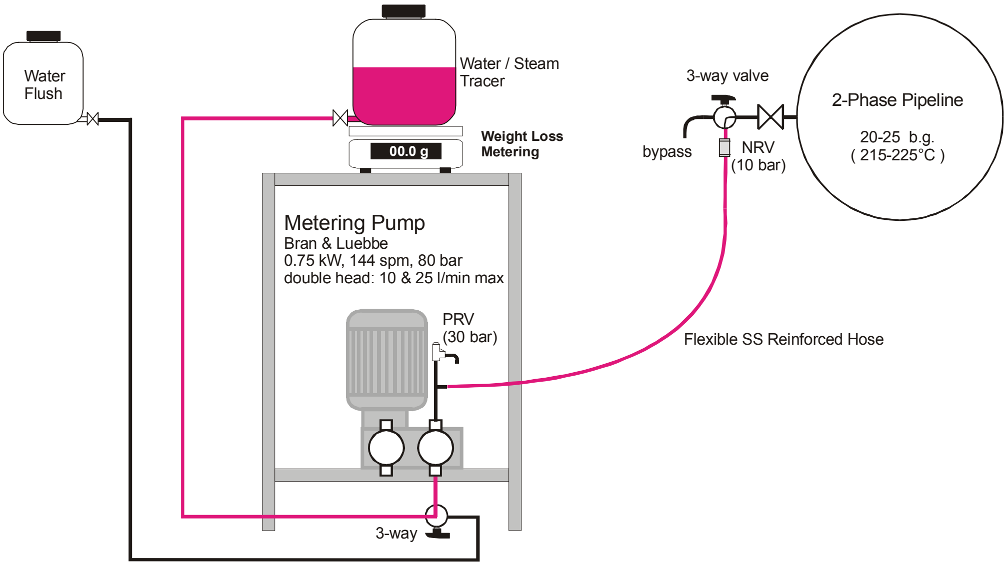

Figure 1. Schematic layout of tracer injection rig

Table 2. Steam flow measurements on well RK5 using alcohol tracers. Sampling pressure = 21 b.g. (mean annubar flow measurements during same period = 119 t/h)

Sample	Date	Time	Tracer	Injection Rate *g/min*	Tracer in Steam *mg/kg*	Tracer in Water *mg/kg*	Steam Flow * *t/h*
D2	17-Jun-99	1120	Isopropanol	110	48.5	3.8	**121**
D3		1125		110	48.5	3.9	**121**
D4		1130		110	48.7	3.8	**120**
E2	17-Jun-99	1202	Isopropanol	130	57.5	4.5	**120**
E3		1206		130	57.5	4.6	**120**
E4		1210		130	57.2	4.5	**121**
I4	16-Jun-99	1310	Isopropanol	84.0	37.2	2.9	**120**
H1	16-Jun-99	1356	Butan-2-ol	98.5	44.0	2.7	**122**
H2		1358		98.5	44.0	2.5	**123**
H3		1400		98.5	44.2	2.7	**121**

* corrected using a water flow of 200 t/h

Table 3. Mass flow dilution measurements using a composite tracer: 40% isopropanol / 10% benzoate. Sampling pressure = 24-26 b.g.

				Tracer	**STEAM PHASE**			**WATER PHASE**	**TOTAL**	
Well	Sample	Date	Time	Injection Rate *g/min*	Isopropanol in Steam *mg/kg*	Isopropanol in Brine *mg/kg*	Steam Flow *t/h*	Water Flow *t/h*	Flow *t/h*	Enthalpy *J/g*
RK9	D1	25-Aug-99	14:20	297	82.4	8.5	69.5	167	236	1521
	D2				81.8	7.5	72.0	167	239	1535
	D3		↓		82.6	7.9	70.3	168	239	1522
	D4		14:37		82.9	7.5	70.9	167	238	1529
						Means:	**70.7**	**167**	**238**	**1527**
RK9	E1	26-Aug-99	10:10	297	82.6	8.1	69.5	169	239	1515
	E2				83.3	7.6	69.9	169	239	1517
	E3		↓		82.9	8.3	68.8	169	238	1511
	E4		10:26		83.6	8.0	68.6	173	241	1503
						Means:	**69.2**	**170**	**239**	**1512**
RK5	F1	26-Aug-99	13:06	296	78.2	7.6	74.1	172	246	1526
	F2				78.1	8.0	73.7	169	243	1531
	F3		↓		78.9	8.3	72.3	169	241	1523
	F4				81.8	8.7	68.8	169	238	1505
	F5		13:23		83.9	7.8	68.9	171	240	1501
						Means:	**71.6**	**170**	**242**	**1517**
Total Flow by Tracers (26-Aug-99) :						**RK5 + RK9:**	**141**			
Total Flow at Station (26-Aug-99) :							**140-143**			