UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

SELECTING AND COLLECTING/WATER SAMPLES FROM THERMAL SPRINGS FOR CHEMICAL ANALYSIS:
A METHOD FOR FIELD PERSONNEL

By

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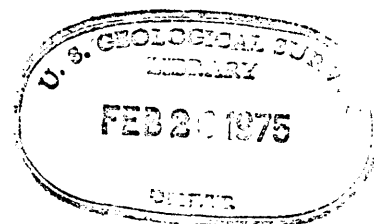
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This report is preliminary and has
not been edited or reviewed for
conformity with Geological Survey
standards and nomenclature.

INTRODUCTION

Water samples of hot springs can be collected and analyzed to obtain data for estimating subsurface aquifer temperatures. Unfortunately, there are very few published guidelines to assist a field geologist in selecting and sampling a thermal spring (see, for instance, Ellis et al., 1968). This paper is an attempt to fill that void.

Presser and Barnes (1974) have described methods of analysis for numerous chemical parameters that should be determined in the field in order to produce a complete, high quality chemical analysis. Major and trace element ions are determined in the laboratory. This type of detailed analysis is mandatory if the data are used to determine the mineral (or rock)-water equilibrium. However, this type of detailed analysis is not essential for hydrogeothermometry; another type of analysis, a major ion analysis, showing a complete range in temperatures, salinities, and discharge rates is sufficient (a major ion analysis allows for a cation-anion balance check to insure that all major constituents have been determined). For the purpose here, a major ion analysis should include the cations (sodium, potassium, lithium, calcium, and magnesium), the anions (carbonate, bicarbonate, sulfate, chloride, and fluoride), plus boron, silica, and pH. A major ion analysis does not yield as accurate or complete an analysis as the first, but since the methods of both types of analysis are the same, the precision of the individual component analyses should also be the same.

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larger the rate of discharge the better. Non-flowing pools (with or
without discharging gas) yield data that are difficult to interpret.
Large pools of low discharge may also be concentrating the constituent
in the water by evaporation or minerals may be precipitating so that the
chemical analysis is not representative of the upflowing subsurface
water. Normally, springs having surface inflow from other springs should
not be sampled. However, if the rate of discharge from the spring is
much greater than the rate of surface inflow, the spring may be nearly
representative of the subsurface upflow. Presence or absence of gas is
not a critical parameter, but it should be noted (this is an important
parameter if the area is considered for more extensive sampling). If
possible, sample springs with a neutral to alkaline pH (pH 6 to 9). Mud
pots, mud volcanoes, and turbid acid springs are usually quite difficult
to filter and chemical analyses of their "major" ions as discussed here
yield no useful geothermometry information. These thermal features
generally have water compositions which are controlled, at least in part,
by the acid leaching of the surrounding rocks.

SAMPLING PROCEDURE

Three bottles of water should normally be collected at each spring
or sampling site: one filtered acidified, one filtered only, and one
diluted for SiO_2. The procedure is initiated by thoroughly rinsing the
syringe with spring water and then filling the syringe. The Swinnex
filter unit is attached and approximately 15 ml of sample is filtered to
rinse the Swinnex filter unit. The remaining volume is filtered and used

to rinse the sample bottles and caps. The filter unit is removed and the syringe is refilled. The filter unit is then replaced and the sample filtered into a 60 ml sample bottle. When the bottle is nearly full, the sample is acidified to pH <2 (six drops of acid should be sufficient; confirm with the pHydrion pH paper). This sample is for cation analysis.

This first sample is filtered and then acidified to prevent suspended solids and colloidal material from dissolving and contributing to the cation concentrations. Filtration prevents clogging of the aspirator on an atomic absorption spectrometer (AAS) and removes suspended solids and organic material that may clog pipettes and disturb spectrophotometer readings. Acidification also prevents reactions which may precipitate calcium carbonate, calcium sulfate, and magnesium carbonate after sample collection.

The above procedure is repeated to fill the 250 ml bottle. This second sample must not be acidified and is for anion analysis. This sample is filtered to prohibit algae growth in the bottle. A 0.45 μm filter is usually sufficient to remove most Protista.

A silica sample is taken by pipetting 10 ml of spring water into the bottle containing 50 ml of silica-free water (distilled-deionized or deionized-distilled water is suggested). It is imperative that the cap on this sample not leak. Diluting the sample water insures a silica concentration sufficiently low so that polymerization of silica is prevented. Suspended silicate solids dissolve slowly in natural water (pH 6 to 9) at low temperature, so that filtration is not required. Suspended colloidal amorphous SiO_2 may dissolve. This is actually

desirable since the silica concentration determined will be closer to the true silica concentration and will indicate a geothermometer temperature closer to the actual aquifer temperature.

After laboratory analysis, the investigator may refer to Table II (modified from Truesdell, 1974b) which is a summary of information obtained by chemical analysis of hydrothermal systems. In general, the data may also be used as indicators of subsurface temperature (e.g. Fournier and Rowe, 1966; Fournier and Truesdell, 1970; Mahon, 1970; Truesdell, 1974a). Should any samples indicate a geothermally interesting area, additional comprehensive sampling should be done by specialists more familiar with field collection and analysis techniques for trace element analysis, for gas analysis, and for non-radioactive isotope studies.

Table I

Equipment	Purpose
1. Maximum reading mercury in glass thermometer for hot and warm springs	To ascertain spring temperature
2. Conventional mercury in glass thermometer for cold springs	To ascertain spring temperature
3. A box of high quality, non-bleeding, pH indicating strips that respond in low ionic strength solutions (e.g. E. Merck Spezialindikator) or a pH meter and pH 7 buffer	To determine spring pH
4. A device to submerge a bottle in a boiling or very hot spring (e.g. a pair of tongs or a clamp)	To prevent scalding fingers and hands
5. Empty plastic sample bottles, 60 and 250 ml volume with appropriate tight sealing cap (e.g. polyseal caps)	To contain water sample and prevent spilling loss
6. A 60 ml plastic bottle containing 50 ml of silica-free water	To dilute silica sample so that poly-merization does not occur

Table I.--Cont.

	Equipment	Purpose
7.	Plastic 10 ml pipette	To obtain silica sample
8.	Large plastic syringe, 50-60 ml capacity, with Luer lock	To collect and filter water sample
9.	A plastic Swinnex filter unit with either 0.22 or 0.45 μm pore size with extra filters	To filter water samples
10.	A roll of pH paper (e.g. pHydrion paper 1-5.5)	To check pH of filtered-acidified sample
11.	Bottle of 1:1 HCl with dropper	To acidify water sample
12.	Bottle of Quantab chloride indicators (#1175)	To test for chloride
13.	A dozen 50 ml or smaller plastic beakers	To hold spring sample for Quantab chloride indicator
14.	A 60 or 125 ml glass bottle (optional but useful)	To collect an isotope sample

Table II.--Importance of individual components of water and gases in

chemical study of geothermal system

Cl   Not affected by water-rock reaction in near surface; critical

            for differentiating hot-water and vapor-dominated systems;

            critical for determining subsurface dilution. Mixing is

            generally indicated if the Cl concentration difference between

            the highest and lowest exceeds 10-15%.

B   Not affected by water-rock reaction in near surface;

            relatively high in thermal water, especially those from

            sedimentary rocks. Can often be substituted for Cl in

            mixing calculations.

Cl/B   Usually distinctive for each mass of thermal water; can

            indicate deep interconnections and mixture of water masses.

            Consistency of ratio indicates a homogeneous source for the

            most soluble constituents.

Na, K, Ca   Strongly affected by temperature-dependent water-rock reactions

            (especially K and Ca); used as a geothermometer.[*]

SiO_2 Strongly dependent on subsurface reaction with silica

            minerals and silicates; used as a geothermometer.[*]

$Cl/(HCO_3-CO_3)$ Strongly dependent on CO_2-water-reactions that depend

            on temperature, CO_2 pressure, and reactive reservoir rocks;

            useful as an index to subsurface flow; change by a factor of

            8 observed in a single system.

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Table II.--<u>Importance of individual components of water and gases in</u>

<u>chemical study of geothermal system</u>--Cont.

Na/Li   Qualitative index to geothermal quality; ratio is between

60 and 80 in high temperature systems; up to 1500 in normal

waters.[*]

Mg   Qualitative index to geothermal quality; very low in high

temperature systems of low salinity.[*]

SO_4 Of both deep and near surface origin (from oxidation of H_2S),

high SO_4/Cl commonly indicates steam fed springs.

pH   Usually low in steam fed springs if H_2S is available for

oxidation to SO_4 (in one case the pH is 1); field measurement

allows calculation of $HCO_3 - CO_3$ distribution.

Temperature   Valuable for calculation of heat flow and subsurface mixture

and for estimation of subsurface flow pattern.[*]

Discharge   Valuable for evaluating significance of temperature; also for

indicating if much heat is lost by conduction. Important to

estimate discharge of individually sampled springs as well as

the surface discharge of each system. Valuable in estimating

heat flows.

[*]/From Truesdell (1974b)

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