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CHEMICAL ANALYSES OF GEOTHERMAL WATERS AND STRATEGIC PETROLEUM RESERVE BRINES FOR STRATEGIC AND PRECIOUS METALS

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ABSTRACT

Waters from seven hydrothermal-geothermal, one geopressured-geothermal, and six Strategic Petroleum Reserve wells have been surveyed for twelve metals of special strategic and economic importance using trace chemical analysis techniques. The elements sought were Cr, Co, Mn, Ta, Sn, V, Nb, Li, Sr, Pt, Au, and Ag. Platinum was found at a concentration of ∿50 ppb in a brine from the Salton Sea geothermal area. Brine from this region, as has been known from previous studies, is also rich in Li, Sr, and Mn. Higher concentrations (∿900 ppm) of Sr are found in the high-salinity geopressured brines. None of the fluids contained interesting concentrations of the other metals. Good recovery of precious metals at sub-ppm concentrations from synthetic high salinity brines was achieved using Amborane reductive resin, but similar recovery in the laboratory using real brines could not be demonstrated. Several analytical techniques were compared in sensitivity for the determination of the precious metals; neutron activation analysis with carrier separation is the best for gold and platinum in geothermal brines.

INTRODUCTION

The significance and implications of U.S. dependence on what are considered strategic materials have received increasing attention recently. These are materials that have widespread essential use in military and industrial hardware, are not found or produced in the U.S. in sufficient quantity to meet the demand, and are likely to be subject to interruptions in supply because of the actions of cartels or political activities. A number of the industrially important metals can be classified as strategic materials, but those of greatest concern are chromium, cobalt, manganese, tantalum, tin, and the platinum metals, particularly platinum itself. A comprehensive, authoritative review of the institutional and technical issues involved in defining the U.S. position with respect to these strategic materials has been published by Maimoni and Borg (1981, 1982).

Possible domestic sources of strategic metals that have not been explored in detail previously are (1) the waters from geothermal wells that are now under active development, (2) the brines produced during the leaching of salt domes on the U.S. Gulf Coast for strategic oil storage, and (3) waters from geopressured-geothermal wells under investigation for methane recovery. Even though the concentrations of strategic metals in these waters may be low, the very large volumes of fluid that are processed and now discarded make them attractive resources, especially if economical hydrometallurgical extraction techniques can also be devised.

Several hydrothermal geothermal fluids, particularly the high-temperature, high-salinity brines, are known to be rich in minerals (Cosner and Apps, 1978; Shannon, 1978), and interest in geothermal mineral recovery along with power generation has been slowly growing

(Maimoni, 1982; Raber et al, 1981; Crane, 1982; Wei, 1982; Schultze and Bauer, 1982). Although several of the geothermal brines have been analyzed for a few of the strategic metals, no concerted effort has been directed toward a more accurate characterization of these fluids in the context of a strategic materials program. Some of the strategic metals are not normally determined in a routine chemical analysis, and the concentration levels of interest for metals such as platinum require very specialized techniques for accurate measurement.

Geopressured-geothermal brines offer another class of potential fluids for mineral recovery. These fluids are being tested at a number of deep wells in Texas and Louisiana, are of interest primarily for their methane content, and their utilization is in an earlier stage of development than the hydrothermal-geothermal resources (Westhusing, 1981). Like some of the mineral-rich hydrothermal fluids, the geopressured brines are also highly saline.

Salt dome leaching is presently being utilized to create large underground caverns for storage applications. The largest scale of such an activity is the U.S. Strategic Petroleum Reserve (SPR) (Davis, 1981), where large quantities of brine are presently discharged into the Gulf of Mexico. A previous preliminary analysis of one of these brines (Raber, et al, 1981) indicated a promising economic concentration of platinum.

In the work described here, a number of hydrothermal-geothermal, one geopressured-geothermal, and several SPR fluids were sampled and analyzed for a suite of strategic metals. The fluid samples were carefully obtained under conditions that assured representative samples. Extra precautions were taken to avoid contamination and to insure stability of the samples prior to analysis, and where possible, each metal was determined by two or more independent analytical facilities or techniques. The principal techniques of analysis were fire assay and neutron activation analysis for the precious metals, and direct spectroscopic analysis of the fluids for the other elements. We also conducted a preliminary study of the use of a reductive resin for the extraction of metals from the high-salinity brines.

FLUIDS SAMPLED AND METALS DETERMINED

Table 1 lists the various sources of the samples of water examined in this study. The principal characteristics of these well fluids have been documented elsewhere in studies dealing with each site. It is of interest in the present work to note that they ranged from the SPR brines, which were saturated in salt (∿26% Total Dissolved Solids), to those of very low dissolved solids (e.g., Wen No. 1, <0.1%). The Sweet Lake geopressured brine and the Elmore No. 2 geothermal brines also are high-salinity fluids (15-22%). The downhole temperatures of the fluids range from the nearly ambient temperature of the SPR brines, through the relatively low temperature geothermal waters such as Wen No. 1 (117°C), to the extremely hot (358°C) Hawaiian well HGP-A.

Because of our multielement analytical capabilities and those of our subcontractors, a number of elements were determined in each water sample. However, the principal elements of interest were the following strategic metals: Chromium (Cr), cobalt (Co), manganese(Mn), tantalum (Ta), tin (Sn), and platinum (Pt). Among this group, tin is the least critical. Because they are of special interest in geothermal mineral recovery, gold (Au), silver (Ag), and lithium (Li) were also determined. Vanadium (V) and niobium (Nb) were added to our list on the basis of criticality and, respectively, low stockpile level and high import reliance (Maimoni and Borg, 1981). Strontium (Sr) also has a high import reliance, but from a relatively stable source, Mexico (Maimoni and Borg, 1981); this metal was included primarily because its concentration is generally relatively high and easy to measure in natural brines.

EXPERIMENTAL

Sampling Procedures

With the exception of one sample (Sulphur Mines 6Z), all of the waters analyzed in this study were obtained from facilities in which the fluid had flowed for a significant length of time prior to sampling. In the case of the new wells (e.g., Elmore No. 2 and Coso No. 75B7) samples were obtained late in the flow test. In the case of the SPR Sulphur Mines No. 6Z, stagnant brine in the well casing was sampled. Wellhead fluid cooled by flow through a cooling coil constituted the samples at Wen No. 1 and Raft River. At Elmore No. 2, East Mesa 6-2, Coso No. 75B7, and HGP-A, samples were obtained from the quench-cooled liquid outputs of the wellhead separators or silencers.

Two types of primary sample containers were used, selected to minimize contamination and loss of trace elements by adsorption (Robertson, 1968, 1972). One was a 4-liter, linear (high-density) polyethylene bottle with polypropylene cap (Nalgene Cat. No. 2125-4000) and the other was a 2-liter FEP-Teflon bottle with ETFE-Teflon cap (Nalgene Cat. No. 1600-0064). These containers were first cleaned by a procedure based on the recommendations of Laxen and Harrison (1981), which consisted of rinsing with water, soaking with 10% HNO_3 for >24h, rinsing, then soaking with 1% HCl for >24h, rinsing, and finally soaking with water for >24h.

Except for some of the samples that were mixed with reductive resins, all of the samples were stabilized immediately after sampling by acidification with hydrochloric acid to a concentration of 1%. The HCl was J. T. Baker high-purity Ultrex grade. In addition, the high salinity and high-silica brines were diluted ~1:1 with high purity distilled water to minimize precipitation of their major and trace components.

All of the waters except those from the SPR sites were perfectly clear in appearance at the time of sampling; however, we did not filter any of the samples prior to stabilization. Our basic philosophy here was to seek particular elements without regard to their chemical state. If promising levels were found, then filtered samples could also be tested. In addition, promptness of stabilization of the sample was important; it is possible that some species may precipitate or be adsorbed on precipitates during filtrations and be lost.

Evaporation of Brines

To prepare the samples for fire assay, portions of the high-salinity brines were evaporated to the dry salts using the apparatus shown in Figure 1. The containers were Fluoroware, Inc. Type E13, 2500-ml PFA-Teflon conical tanks, which were used as both the top and bottom of the evaporation chamber. The hot plate control was set to give a surface temperature of 150°C. Except for an ocean water blank, 1-2 kg of brine was evaporated to yield 250-400 g of salt. After the evaporation, the salts were broken up and removed to sample bottles using a Kel-F chisel and Teflon forceps. The salts were not further crushed or homogenized. All of this apparatus was cleaned with 10% HNO_3.

Reaction of Waters with Amborane Resin

Each of the waters except the Sweet Lake geopressured brine was reacted with Rohm and Haas Company Amborane-355 reductive resin (Rohm and Haas, 1980; Manziek, 1982). A weighed portion of ~32 g of Amborane was added to one of the 4-liter bottles of water immediately after sampling at the wellhead and mixed thoroughly. The mixture was agitated naturally in transit to the Lawrence Livermore National Laboratory; subsequently, the bottles were placed on rollers and subjected to additional mixing for 4 hours. At least one week elapsed between the time of fluid sampling and final filtration of the resin.

The Amborane resin was removed from the waters by vacuum filtration through a 110-mm, coarse Teflon filter in a polypropylene Buchner funnel. The resin was rinsed with water several times and dried under vacuum in the funnel. The final weights of each resin sample prepared in this manner ranged from 34-72 g. Prior to use, the Teflon filters were leached with 10% HCl and the funnels cleaned with 10% HNO_3.

Standard Solution Preparation

Standard solutions of platinum, gold, and silver were prepared from, respectively, Spex No. AQPT-3-100 spectrographic standard solution, Marz-grade Au wire, and reagent-grade $AgNO_3$ salt. Aliquots of these solutions were added to various synthetic brines prepared to ascertain the recovery obtained in the evaporation/fire assay and the reaction with Amborane resin. In each of these experiments, 4-liter batches of synthetic brine prepared from Ultrex or reagent-grade NaCl and KCl were spiked with the appropriate quantities of the Pt, Au, and Ag solutions.

Chemical Analysis Procedures

The precious metals Pt, Au, and Ag were each determined by several methods. One technique involved a fire assay (Beamish and Van Loon, 1977) of the evaporated salts from the high-salinity brines. In this technique, for highest sensitivity, Pt and Ag were collected in Au and measured, respectively, by emission spectrography and atomic absorption spectrophotometry. Gold was determined by collection in Ag followed by atomic absorption spectrophotometry. The Amborane resin beads were also subjected to a fire assay for Pt, Au, and Ag after roasting in air. The fire assay determinations were performed by Ledoux and Company of Teaneck, New Jersey.

The samples were also surveyed for strategic metals by neutron activation analysis (Guinn, 1971). General Activation Analysis of San Diego assayed all of the liquid samples for Au and Pt using the following procedure. The samples plus comparator standards were irradiated for 30 min. in a TRIGA Mark I nuclear reactor at a flux of 1.8×10^{12} n/cm^2-sec. After a decay of 3 days they were wet-ashed in the presence of Au carrier. Gold was then separated as the element and counted with a Ge(Li) detector coupled to a multichannel gamma-ray spectrometer. The Au-198 and Au-199 isotopes thus measured in the irradiated sample corresponded to the Au and Pt, respectively, in the original water sample. Silver in the Elmore No. 2 brine was determined by directly counting a sample of the original, irradiated brine after a delay of 3 months.

Manganese, Sr, Co, V, and Li were determined by inductively-coupled-plasma emission spectrometry (Peck, et al, 1979). Tin, Cr, Nb, and Ta were determined using a Spectrametrics, Inc. DC-Plasma Spectrospan system.

RESULTS AND DISCUSSION

Non-Precious Metals Analyses

Table 2 summarizes the results of the analyses of the collected waters for all of the elements of interest except the precious metals, Au, Ag and Pt. For all of the fluids, the concentrations of Co, Sn, Cr, and V were very low or undetected at the parts-per-million level. No Nb or Ta was found either, but the detection limits for these elements were relatively higher, especially for the high-salinity brines where spectral interferences and other matrix effects make these determinations less sensitive. Separation of the Nb or Ta prior to measurement appears to be required for a more accurate analysis at the levels that may exist. The Strategic Petroleum Reserve brines are generally devoid of interesting concentrations of all of the metals sought, including the precious metals.

As has been evident from previous studies and compilations of data (Austin, et al, 1977; Cosner and Apps, 1978; Maimoni, 1982; Shannon, 1978), the higher salinity geothermal and geopressured-geothermal (Karkalits and Hankins, 1981; Kharaka, et al, 1979) brines do contain significant concentrations of Li and Sr. Lithium has been the subject of efforts in mineral recovery at the Cerro Prieto, Mexico, facility where its fluid concentrations are also high (Mercado, et al, 1979). A survey of the results of the analyses of the fluids of a number of wells in the Salton Sea KGRA (Austin, et al, 1977; Cosner and Apps, 1978; Shannon, 1978) shows that the concentration of Sr is in the range of 300-500 ppm. Interestingly, the somewhat lower-salinity geopressured-geothermal brines contain twice as much Sr (Karkalits and Hankins, 1981; Kharaka et al, 1979), and might be useful sources of this element. The high concentrations of Mn in the Salton Sea KGRA brines, in the range of 1000 ppm (Austin, et al, 1977; Cosner and Apps, 1978; Shannon, 1978), have stimulated several recent mineral recovery studies (Crane, 1982; Farley et al, 1981; Maimoni, 1982; Schultze and Bauer, 1982).

Precious Metals Analyses

Table 3 summarizes the results of fire assay analyses performed on the solids obtained by evaporation of the various high-salinity brines. This method was chosen because the high-salinity brines could easily be concentrated by a factor of 4-5 in this manner, and fire assay is widely regarded as the most reliable technique for the analysis of solids such as ores for the precious metals.

As noted in Table 3, three types of blanks were subjected to analysis. One was a 20% solution of ACS reagent-grade NaCl; one was a solution that was 15% in NaCl and 4% in KCl, both of which were Ultrex-grade salts, and one was a sample of Pacific Ocean water obtained several miles off the California coast. None of these samples were expected to contain measurable levels of Ag, Au, or Pt. The reported results for these elements indicate apparent background levels of ~1.4, ~0.4, and ~0.1 ppm, respectively, for Ag, Au, and Pt in the evaporated solids. For a 20 wt.% brine, these values are equivalent to concentrations of, respectively, 0.3, 0.08, and 0.02 ppm in the liquid. Almost all of the brine samples yielded results for silver, gold, and platinum that were indistinguishable from those for the true blanks. We thus used these values to calculate a more accurate value for the mean and standard deviation of the blanks, and from these, limits of detection of the evaporation/fire-assay method. Listed in Table 3 are the mean values of the blanks and limits of detection (LOD) calculated from LOD = $\bar{b} + 3s$, where $\bar{b}$ is the mean value of the blank and s is its standard deviation (American Chemical Society Committee, 1980; Koch, et al 1982).

All of the results of the brine analyses were then corrected for the mean values of the blanks determined in this manner.

As shown in Table 3, the experiment with the standard revealed that concentrations of Ag, Au, and Pt 2-3 times the background levels were easily detected. This standard, in addition to the spiked amounts of Ag, Au, and Pt, contained 14% Ultrex NaCl and 3% Ultrex KCl to simulate a high-salinity brine. Recovery values for the standard are ∿100%, ∿100%, and ∿50%, respectively for Ag, Au, and Pt. However, these values must be regarded with some uncertainty because only one standard was analyzed. Among the fire assays of these brines, only the result for Pt in Elmore No. 2 is significantly higher than the limit of detection.

As the primary assay of the low-salinity geothermal fluids, and as a second, independent analysis of the high-salinity brines, the samples were also analyzed directly by neutron activation analysis. As described above, this technique is a highly-selective carrier precipitation that separates the Au and Pt from the other constituents prior to measurement. It is extremely sensitive for Au, and only high concentrations of Au would interfere with the Pt determination.

The concentrations of Au and Pt in the fluids that were calculated from the results obtained by neutron activation analysis are listed in Table 4. As in the fire assay, about one-half of these analyses were performed on diluted brine, and the values listed in Table 4 have been corrected for this dilution. The effective mean blank and limit-of-detection values were also calculated for these data as described for the fire assays, and these results are also listed in Table 4. For most of these analyses, the concentrations of Au and Pt were less than the inherent detection limits of the radioactivity counting technique.

Correcting the two positive results for the mean blank values yields values for 0.06 ppb Au for the Raft River No. 1 water and 51 ppb Pt for the Elmore No. 2 brine. The latter result thus tends to confirm the fire assay value for Pt in this brine. The lower value for Pt obtained by evaporation/fire assay, 12 ppb, could have come from losses in the extensive sample processing involved in this procedure; analysis of the standard for Pt also did not yield a quantitative recovery.

Silver was not initially determined by the neutron activation technique because accurate results would have required an additional separation. However, after a delay of 3 months to allow the radioactivity to decay, when a more favorable signal could be obtained, the Elmore, No. 2 sample was counted and estimated to contain (in the original brine) 45 ± 23 ppb Ag. This value, although accompanied by a fairly large uncertainty, is lower by a factor of 10 than most values previously reported for Salton Sea KGRA brines (Austin, et al, 1977; Cosner and Apps, 1978; Shannon, 1978). This result is in agreement with a study conducted at SRI International (Farley et al, 1981), which showed that many previous analyses of such brines by direct AAS without background correction may be in error due to matrix interferences. These investigators found a value of 20 ppb for Magmamax No. 1 brine after dithizone/solvent extraction. Thus, although Ag is indisputably an important constituent of the high-temperature scales (Austin, et al, 1977) and sludges (Featherstone and Powell, 1981) formed by the Salton Sea KGRA brines, its concentration in the fluid itself may not be as high as previously believed.

In the present study, each of the low-salinity waters (EM6-2, C75B7, HGP-A, RR1, RR3, and W1) were analyzed by direct AAS, but no silver was found above the limit of detection of 20 ppb.

Amborane Resin Extractions

Experiments were performed to determine whether the precious metals could be extracted from the brines using a resin, Amborane-355, which is specific for elements low in the electromotive series, i.e., those that are relatively easy to reduce to the metals. The resin is a polymeric amine-borane resin, and is a relatively mild reducing agent, thus is quite selective for gold, silver, and the platinum metals (Rohm and Haas, 1980; Manziek, 1982). Our experiments had a twofold objective. First, if the resin proved effective in the case of our brines, the extraction would afford a preconcentration for the fire assay and thus a much greater sensitivity in the overall analysis. In addition, if the extraction recovery proved high, the resin might be considered promising in larger-scale mineral recovery processes.

The results of the reductive-resin metal recovery experiments are given in Table 5 for the various fluids that were sampled. A portion of the as-received resin was also submitted as a blank for the fire-assay analysis. Because the weight of resin used was ∿30g, and the quantity of original fluid contacted was 2-4 kg, a potential preconcentration factor of ∿100 was operative.

The effective mean blank values and limits of detection were also calculated for this method as described above and these values are also listed in Table 5. The only result for a water that exceeds the LOD is that for gold in Coso Hot Springs 75B7. correcting for the blank yields a concentration of 27 ppb; however, this result was not confirmed by the neutron activation analysis of this water (see Table 4). Note that although the other two methods detected platinum in the Elmore No. 2 brine, none was recovered in this resin recovery experiment. The large preconcentration factor yields a fairly good overall sensitivity for Pt and Au, but not for Ag, where there is a relatively high background of 5-6 ppm for the resin itself.

A series of experiments was also conducted using synthetic brines spiked with the precious metals to determine effect of pH, salinity, and equilibration time on the recovery of the metals. Of particular concern to us was the recent report by Manziek (1982) on the recovery of platinum from chloride solutions. He found that recoveries of platinum at the 1000-ppm level were good for short contact times; but on prolonged standing of the resin with the solution, the platinum was reoxidized and leached from the resin, especially when gold was also present. In our experiments we used a much higher concentration of chloride, and much lower concentrations of the precious metals--∿0.5 ppm Ag, ∿0.09 ppm Au, and ∿0.05 ppb Pt in the solution. The results are summarized in Table 6.

There was reasonably good recovery under all conditions for Ag and Au, and excellent recovery for Pt. There were no replicates, thus the statistical uncertainties are unknown, but it appears that the metal recoveries are not particularly sensitive to pH or chloride concentration. Because it was thought initially that the resin/brine equilibration time might have had an effect on the recovery of Pt, another experiment was done with aged Elmore No. 2 brine in which the resin was allowed to contact the brine for only 1 hour before filtration. However, the concentration of Pt reported for the resin from this experiment was not significantly above that of the blank.

There still remains the question of whether the Amborane resin can extract trace amounts of the precious metals, particularly Pt, from the real brines. As Manziek (1982) has shown, Pt is sensitive to reoxidation, and our simulated brines lacked one constituentof real brines, iron, which might be capable of effecting this reaction. The Elmore No. 2 geothermal brine contains ∿570 ppm iron, which is initially present largely as Fe^{2+} in the anoxic fluid. This ferrous iron would not be a factor in the reoxidation; however, on sampling and storing the brine under normal conditions, the brine becomes aerated, Fe^{2+} is oxidized to Fe^{3+}, and then Fe^{3+} might be capable of reoxidizing constituents in the resin. In any event, further experiments would be required to confirm such a reaction, and if important, steps could be taken in mineral recovery processes to avoid allowing aeration of the fluid in the flow system.

COMPARISON OF ANALYTICAL METHODS

It is of interest to compare in more detail the sensitivities of the three analytical methods that were used to measure the concentration of precious metals in the water samples. Table 7 summarizes, for each of the techniques, and each of the precious metals, the mean blank, its standard deviation, and a limit of detection (LOD), calculated as described above. Also listed is the calculated limit of quantitation (LOQ), which is defined as a level above the blank ten times the standard deviation of the blank (ACS Committee, 1980; Koch, et al, 1982).

For the fire assays of the evaporated solids, the LOD and LOQ values were calculated for a typical high-salinity brine, in which evaporation would result in a concentration factor of ∿5. For the extraction with Amborane resin, a preconcentration factor of 100 was assumed. The neutron activation analysis technique is assumed to be applied directly to the original water samples, some of which were diluted in our study.

Neutron activation analysis is clearly the most sensitive technique for the determination of gold (and for silver, as well, based on the one measurement of Elmore No. 2 brine.) The levels of the blanks are too high for the fire assays of either the solids or the resins to be useful for the measurement of silver. Atomic absorption spectrophotometry without preconcentration by solvent extraction is also probably inadequate for silver, if the allowable variability of the blank is considered.

For platinum, the large preconcentration factor afforded by the resin extraction, together with the high sensitivity of the fire assay with spectrographic finish, make this technique, in theory, the most sensitive. A limit of detection of ∿2 ppb appears possible, and was virtually achieved in the recovery studies with synthetic brines (see Table 6). This fact, however, begs the question of why the platinum detected in the Elmore No. 2 brine by the other two techniques was not removed by the resin extraction. Be that as it may, neutron activation analysis with carrier precipitation emerges as more attractive in the present application because of its greater simplicity and adequate sensitivity. Of course, there is a wealth of other trace analysis techniques in the literature that may also be suitable for determining these precious metals, and as mineral recovery receives increasing emphasis, these alternatives should be investigated.

CONCLUSIONS

The principal finding of this investigation is the presence of Pt at a concentration of ∿50 ppb in a Salton Sea KGRA geothermal brine from the well Elmore No. 2. This is most probably related to hydrothermal alterations of the surrounding country rocks, although it is speculated that these brines are a combination of magmatic and meteoric origin. Platinum was detected by two different analytical techniques: fire assay of the evaporated salts and carrier precipitation/neutron activation analysis. However, attempts to extract the platinum (and other precious metals) from this and other geothermal and SPR brines using a reductive resin yielded negative results, even though simulated NaCl brines were shown to be amenable to this approach. Further laboratory and field studies should be performed to determine the effects of some of the minor constituents in such brines on the recovery of precious metals by this technique. Other techniques such as electrolytic extraction and the use of activated carbon should also be investigated. If possible, other samples of geothermal fluids should be obtained from other wells at the Salton Sea KGRA to confirm and assess the extent of Pt in this resource.

Among the other strategic metals of primary interest: Cr, Co, Sn, and Ta could not be detected in any of the fluids. Chromium and Co concentrations are below 0.5 ppm, and Sn is below 1 ppm. The analytical sensitivity for Ta was poor for the technique used, 1-12 ppm. As was known from previous studies, the concentration of Mn in the Salton Sea KGRA brine is very high, ∿1000 ppm or more, and at the present time this element is of considerable interest from the point of view of mineral recovery. A determination of Ag that yielded a value of 45 ± 23 ppb for the Elmore No. 2 brine lends support to the contention that the higher values previously found for many Salton Sea KGRA brines are in error.

For the high-salinity brines, in which significant concentrations of precious metals are more likely to be found, the limit of detection of the fire assay as applied to the evaporated solids is not low enough for accurate determinations of the precious metals. Limits of detection (3σ) of 0.5 ppm Ag, 0.14 ppm Au, and 0.026 ppm Pt were established for this technique. Atomic absorption spectrophotometry with preconcentration by solvent extraction appears to be a better technique for Ag. Neutron activation analysis with carrier precipitation is the best technique for Au and Pt, except when the ratio of Au:Pt is excessive. This technique will yield limits of detection of ∿0.04 ppb Au and ∿7 ppb Pt in the original fluid. For Pt, extraction with Amborane resin and fire assay of the dried resin is capable of a limit of detection of 2 ppb, but it has yet to be demonstrated with a real brine.

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TABLE 1. Waters sampled for strategic metals

Well	Developer/Owner	Location/KGRA[a]	Water Designation	Approximate Total Dissolved Solids, wt. %
Strategic Petroleum Reserve				
No. 106A	U.S.D.O.E.[b]	Bryan Mound, TX	BM106A	26
No. 110C	U.S.D.O.E.	Bryan Mound, TX	BM110C	26
No. 101	U.S.D.O.E.	West Hackberry, LA	WH101	25
Nos. 8A & B[c]	U.S.D.O.E.	West Hackberry, LA	WH8A8B	26
No. 7C	U.S.D.O.E.	Sulphur Mines, LA	SM7C	26
No. 6Z	U.S.D.O.E.	Sulphur Mines, LA	SM6Z	27
Geopressured-Geothermal				
Amoco Fee No. 1	Magma, Gulf-Technadril/ U.S.D.O.E.	Sweet Lake, LA	SL1	15
Geothermal				
Elmore No. 2	Magma Power Co.	Salton Sea, CA	E2	21
No. 6-2	U.S.D.O.E.	East Mesa, CA	EM6-2	0.5
No. 75B7	Cal Energy Inc./ U.S. Navy	Coso Hot Springs, CA	C75B7	1
HGP-A	Hawaiian Electric Co./ U.S.D.O.E.	Puna, HI	HGP-A	1
No. 1	U.S.D.O.E.	Raft River, ID	RR1	0.16
No. 3	U.S.D.O.E.	Raft River, ID	RR3	0.4
Wen No. 1	Geoproducts Co.	Wendel-Amedee, CA	W1	0.13

[a] Known Geothermal Resource Area

[b] United States Department of Energy

[c] Composite sample

TABLE 2. Results of chemical analyses of waters for non-precious metals by spectroscopic methods

	Metal Concentration, mg/kg (ppm by wt.)								
Water[a]	Li	Sr	Co	Mn	Sn	Cr	V	Nb	Ta
Strategic Petroleum Reserve									
BM106A	0.25	2.0	<0.37	<0.03	<0.8	<0.2	<0.15	<3	<12
BM110C	0.21	2.2	<0.40	<0.03	<0.8	<0.2	<0.16	<3	<12
WH101	<0.12	2.1	<0.30	<0.02	<0.7	<0.2	<0.12	<3	<12
WH8A8B	<0.11	2.4	<0.30	<0.02	<0.3	<0.2	<0.11	<3	<5
SM7C	<0.18	1.4	<0.44	<0.04	<0.4	<0.2	<0.18	<4	<3
SM6Z	<0.16	1.2	<0.40	<0.03	<0.4	<0.1	<0.16	<4	<4
Geopressured-Geothermal									
SL1	36	860	<0.50	15	<2	<0.1	0.3	<10	<10
Geothermal									
E2	132	301	0.43	995	<2	<0.2	1.1	<6	<15
EM6-2	4.3	2.0	<0.005	0.005	<0.1	<0.1	<0.002	<0.1	<1
C75B7	25	3.7	0.008	0.007	<0.2	<0.2	0.010	<0.2	<2
HGP-A	0.034	2.0	0.014	0.034	<0.2	<0.2	0.016	<0.4	<2
RR1	1.5	1.3	<0.005	0.003	<0.1	<0.1	<0.002	<0.1	<1
RR3	2.5	3.9	<0.005	0.025	<0.1	<0.1	0.007	<0.3	<1
W1	0.23	0.74	<0.005	0.002	<0.1	<0.1	<0.003	<0.1	<1

[a] See Table 1 for sample code.

TABLE 3. Results of fire assays of solids from evaporation of brines

		Reported Conc. in Solids, mg/kg			Calculated Conc. in Brine, mg/kg		
Water	Sample Type	Ag	Au	Pt	Ag	Au	Pt
	Test Samples						
SB1	Blank, ACS Reag. NaCl	1.4	0.31	0.10	--	--	--
SB2	Blank, Ultrex NaCl, KCl	1.4	0.31	0.10	--	--	--
SA	Blank, Ocean Water	0.9	0.31	0.10	--	--	--
SS1	Standard	4.3	1.07	0.28	0.55	0.113	0.033
	Prepared to Contain:	2.8	0.66	0.40	0.49	0.114	0.070
	Brine Samples[a]						
BM106A	SPR Brine	1.6	0.51	0.07	<0.6	<0.17	<0.033
BM110C	"	1.2	0.34	0.10	<0.6	<0.17	<0.033
WH101	"	1.3	0.41	0.07	<0.6	<0.17	<0.033
WH8A8B	"	1.7	0.55	0.07	<0.6	<0.17	<0.033
SM7C	"	1.8	0.45	0.07	<0.6	<0.17	<0.033
SM6Z	"	1.3	0.45	0.07	<0.6	<0.17	<0.033
SL1	Geopressured-Geothermal	--	0.50	<0.02	--	<0.10	<0.020
E2	Hydrothermal-Geothermal	1.8	0.35	0.14	<0.05	<0.14	0.012
Mean Blank		1.4	0.41	0.083			
Limit of Detection[b]		2.3	0.68	0.13			

[a] See Table 1 for sample code.

[b] Mean blank + 3 x (standard deviation of blank)

TABLE 4. Results of neutron activation analysis of waters for gold and platinum

Water[a]	Metal Concentration, μg/kg (ppb by wt.) Au	Pt
Blank, 1% HCl	<0.02	<5
BM106A	<0.03	<5
BM110C	<0.03	<6
WH101	<0.07	<6
WH8A8B	<0.03	<5
SM7C	<0.03	<7
SM6Z	<0.02	<5
SL1	<0.02	<10
E2	<0.06	55
EM6-2	<0.02	<4
C75B7	<0.04	<11
HGP-A	<0.04	<6
RR1	0.082	<5
RR3	<0.02	<5
W1	<0.02	<3
Mean Blank	0.023	4
Limit of Detection	0.05	7

[a] See Table 1 for sample code

TABLE 5. Results of fire assays of Amborane resins after contacting brines. (Original water samples undiluted and unacidifed except as noted.)

		Reported Conc. in Resin, mg/kg			Calculated Conc. in Brine, μg/kg (ppb)		
Water[a]	Sample Type	Ag	Au	Pt	Ag	Au	Pt
	Untreated Resin Blank	6.8	0.99	0.07	--	--	--
BM106A	SPR Brine	6.0	0.99	0.10	<150	<24	<1.5
BM110C	" "	6.0	0.99	0.07	<150	<24	<1.5
WH101	" "	14.9	0.99	0.14	<150	<24	<1.5
WH8A8B	" "	5.8, 9.6	0.99	0.10	<150	<24	<1.5
SM7C	" "	7.5	0.99	0.07	<150	<24	<1.5
E2[b]	Geothermal Brine	7.6	0.89	0.07	<250	<41	<3
EM6-2[c]	" "	--[e]	0.99	0.07	--[e]	<50	<3
C75B7[d]	" "	3.8	2.0	0.07	<240	<39	<3
C75B7[c]	" "	2.7	2.7	<0.03	<260	27	<3
HGP-A[b]	" "	3.6	0.62	<0.03	<280	<46	<3
HGP-A[c]	" "	4.7	0.62	<0.03	<370	<60	<4
RR1[c]	" "	5.0	0.99	0.10	<380	<62	<4
RR3[c]	" "	--[e]	1.10	0.10	--[e]	<67	<4
W1	" "	--[e]	0.99	0.07	--[e]	<31	<2
Mean Blank		6.5	1.1	0.075			
Limit of Detection		16	2.6	0.17			

[a] See Table 1 for sample code.

[b] Original sample acidified only.

[c] Original sample diluted only.

[d] Original sample acidified and diluted.

[e] Contamination in resin analysis.

Table 6. Results of experiments on recovery of precious metals from synthetic brines by Amborane resin
[Conc. of metals added to brine (mg/kg): Ag ~0.5, Au ~0.09, Pt ~0.05; 10-day resin/brine equilibration except as noted.]

	Ag	Au	Pt			
Metals Added (mg):	1.82	0.34	0.21	Ag	Au	Pt
Sample	Metal Recovered, mg			Calculated % Recovery[b]		
10% NaCl, pH 7 Blank	0.14	0.037	0.013			
10% NaCl, 1% HCl + Metals	1.36	0.36	0.24	67	95	108
10% NaCl, pH 7 + Metals	1.08	0.24	0.22	52	60	99
0.5% NaCl, pH 7 + Metals	1.53	0.28	0.25	76	71	113
10% NaCl, 1% HCl + Metals[a]	1.12	0.23	0.23	54	57	103

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[a] 1-h resin/brine equilibration.

[b] Corrected for blank

TABLE 7. Comparison of capabilities of analytical methods in the detection and determination of precious metals in brines [metal concentrations in mg/kg (ppm)]

Fire Assays of Evaporated Solids

	Ag	Au	Pt
Mean Blank, $\bar{b}$,	1.4	0.41	0.083
Standard Deviation of Blank, s	0.3	0.09	0.016
LOD[a] in 20% brine	0.5	0.14	0.026
LOQ[b] in 20% brine	0.9	0.26	0.049

Extraction, Fire Assay of Amborane Resin

	Ag	Au	Pt
Mean Blank, $\bar{b}$	6.5	1.1	0.075
Standard Deviation of Blank, s	3.2	0.5	0.03
LOD in water; 100X preconc.	0.16	0.03	0.002
LOQ in water; 100X preconc.	0.39	0.06	0.004

Neutron Activation Analysis with Carrier Precipitation

(Undiluted samples)	Ag	Au	Pt
Mean Blank, $\bar{b}$	--	0.000023	0.0041
Standard Deviation of Blank, s	--	0.000008	0.0010
LOD in water	--	0.00005	0.007
LOQ in water	--	0.0001	0.014

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[a] LOD - limit of detection = $\bar{b} + 3s$

[b] LOQ - limit of quantitation = $\bar{b} + 10s$

FIGURE CAPTION

Figure 1. Apparatus for evaporation of brines.

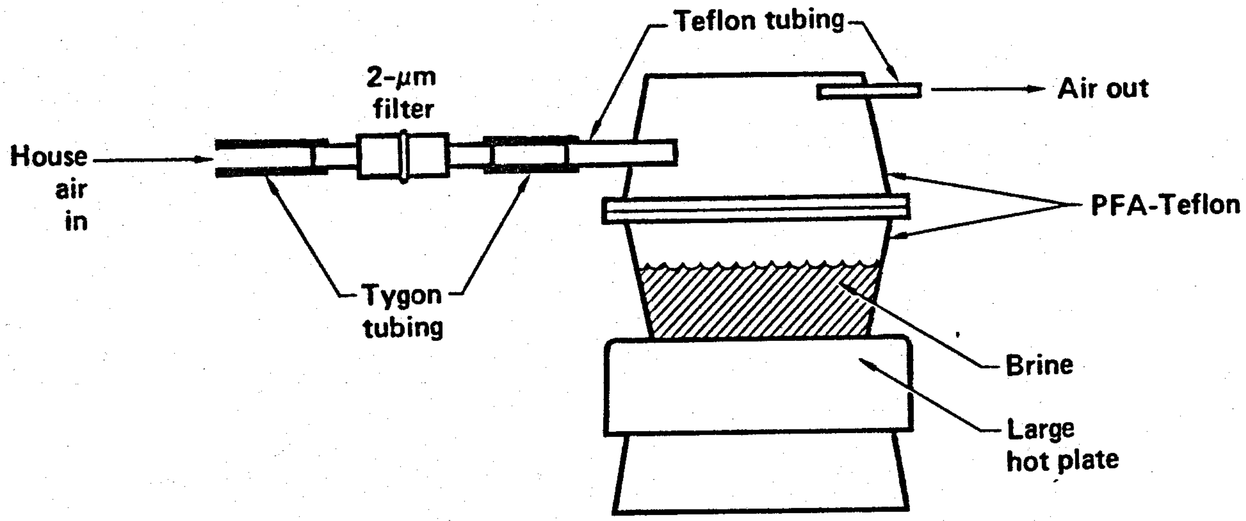

Fig. 1
Harrar
Raber