Regular chemical sampling and analysis of fluids produced from the hot-water geothermal system of Cerro Prieto, Mexico has provided early warning of reservoir processes (Manon et al., 1977). The changes in chloride concentration, sodium to potassium ratio and measured fluid enthalpy are shown in the figures for wells M-5, M-26, M-21A, and M-11 of the Cerro Prieto field. The concentration of chloride, a "conservative" constituent, is characteristic of different water masses and is affected by a change of water source, by mixing of waters and by boiling and steam loss but not by reaction with rock minerals. The ratio of sodium to potassium is a temperature-sensitive geothermal index resulting from rock-water reaction and is not affected by boiling and steam loss or by mixing of water masses provided these processes occur at constant temperature. The enthalpy is related to the fluid temperature and to boiling in the aquifer with "excess" steam entering the well. These indices provide a reasonably complete picture of major reservoir processes occurring in hot water systems. Silica analyses have not been reliable from Cerro Prieto but should be used in addition to Na/K as a temperature indicator. Analysis of fluids from a producing geothermal field must of course include other constituents for study of environmental effects, scaling, corrosion, etc.

Well M-5 at Cerro Prieto shows uncomplicated behavior in which a single liquid phase with little "excess" aquifer steam was tapped and production has shown little change over the life of the well (fig. 1). Before April 1973, initial production was through a small diameter pipe and was cooled conductively so little evaporative concentration of chloride from steam loss occurred and the chloride concentrations of produced fluids approximated that in the aquifer. After April 1973, water was collected from the production separator and flashed to atmospheric pressure during sampling. Steam separation in the separator and during sampling resulted in a 35% loss of water as steam and a 1.6-fold concentration of chloride in the remaining liquid. From 1973 to the present the chloride concentrations after flashing have decreased slightly as the fluid temperature and the amount of steam separated have decreased. The decrease in temperature is indicated by the increase in the Na/K ratios and the decrease in enthalpy. The temperature drop indicated by Na/K was from about 313 ±3°C to 302 ±2°C (the variation depending on the geothermometer scale used) and that indicated by enthalpy was from 312 to 281°C. The larger drop and lower absolute temperature indicated by enthalpy may result from initial excess aquifer steam or from inaccuracies in this rather difficult measurement. The downhole
temperature of 299°C measured in 1977 (F. J. Bermejo, unpublished data, 1977) agrees more nearly with the Na/K temperatures and aquifer chloride concentrations based on Na/K temperatures are more constant (at 8,960 ± 20 mg/kg by one scale) than are those based on enthalpy which show an apparent increase from 8,700 to 9,700 mg/kg.

The other wells show less regular behavior. The chloride concentration after flashing of water from M-26 declined suddenly in mid-1975 indicating drawdown of lower chloride fluids into this part of the production aquifer. Temperatures calculated from Na/K ratios and enthalpies also declined but showed no discontinuity in 1975. This suggests that the fluid temperature was maintained by heat transfer from rock minerals.

Fluids from well-21A had initial enthalpies of 420 to 480 cal/gm equivalent to a temperature of 360 to 370°C if the aquifer fluid were entirely liquid water. The initial chloride concentrations were also unusually high. By 1977 both the enthalpy and the chloride had declined rapidly to values similar to those of M-5 fluids. The Na/K ratio was initially only slightly lower than that of most well fluids but showed a normal increase with time and the Na/K indicated temperature was 315 ± 5°C throughout the period shown. The probable explanation for the unusual behavior of M-21A is that initial fluids contained large amounts of excess steam from boiling in the aquifer and these were replaced with more normal fluids as production continued. The high chloride concentrations resulted from boiling in the aquifer with heat re-supplied to the fluids from rock minerals.

Well M-11 suffered a casing break in 1975 and higher level fluids with lower enthalpy and chloride and much higher Na/K ratio entered the well. When the break was repaired and an upper production interval near 900 m cased off, the well performance was greatly improved, with production of high Cl, high enthalpy, low Na/K fluids similar to early production fluids.

Regular collection and analysis of water (and gas) samples from a hot-water geothermal well is an essential part of a well-testing or monitoring program. The chemical data obtained complements physical measurements and may give the earliest warning of breakthrough of natural or reinjected cold waters. Analyses should be as complete as possible but constituents indicating reservoir processes (Cl, Na, K, Ca, SiO₂) and mineral deposition (pH, HCO₃, CO₂) should be analyzed with special care.

References
Figure 1. Chloride concentrations after flashing, Na/K ratios of brine and enthalpies of the total discharge of wells M-5 and M-26 from 1972 to mid 1977. Data from Manon et al. (1977). Units are mg/kg, weight ratio and Kcal/kg.
Figure 2. Chloride contents after flashing and the sodium to potassium ratio of brine and enthalpy of the total discharge of well M-21A from 1975 to mid-1977 and well M-11 from 1972 to mid-1977. Data from Manon et al. (1977). Units are mg/kg, weight ratio and Kcal/kg.