ARSENIC SPECIATION KIT DEVELOPMENT AND FIELD TESTING IN FOUR NEW MEXICO THERMAL AREAS

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Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Geochemistry

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January, 2002

To my husband Karl
and daughter Stephanie.

ABSTRACT

This paper reports the development of two ion-exchange techniques for separating aqueous arsenic species. The first technique separates arsenite (As(III)) from arsenate (As(V)). Under laboratory conditions, the recovery of As(III) in the eluent is 98.8% ± 23.8%. The recovery of As(V) is 77.0% ± 29.7%. Standards ranged from 2 μg/l to 500 μg/l arsenic. Organic arsenic species coelute with As(III). The two-species separation method works well in the field. For fourteen samples with total arsenic concentrations >10 μg/l, recoveries range from 66.7% to 120.0%, which is good.

The second ion-exchange method separates As(III), As(V), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Recoveries for individual species are comparable to the two-species method, but As(V) is not completely stripped from resin and elutes in the DMA range. Thus, there is false detection of DMA when As(V) is present.

The two-species method was used to gather new data on arsenic species in thermal waters. Four New Mexico regions, Jemez Mountains, Socorro, Bosque del Apache, and Truth or Consequences, were sampled. Total arsenic concentrations in the Jemez Mountains range from 33μg/l to 1100 μg/l. The percentage As(III) ranges from 5.6 to 94.8%. Higher total arsenic sites have greater As(III) proportions. Arsenic correlates positively with chloride, silica, TDS, temperature (33°C to 71°C), and Fe + Mn.

In the Socorro area, arsenic concentrations range from 2 μg/l to 36 μg/l. Arsenic is As(V). The three thermal springs (24.4°C to 33.1°C) contain the highest amount of arsenic in this region. Arsenic is inversely proportional to TDS; there are no correlations with other parameters.

In the Bosque del Apache, arsenic ranges from < 2 μg/l to 20 μg/l. Arsenic is found mainly as As(III), with percentages from 66.7 to 100%. Water temperatures range from 17°C to 32°C. Arsenic shows a negative relationship with TDS and a positive relationship with nitrate in some samples.

Arsenic levels are 2-3 μg/l in the Truth or Consequences area. Measurable species are As(V), but concentrations are mostly too low for speciation. Water temperatures range from 42°C to 44°C. Sample parameters cluster tightly for all samples.

There is no correlation between arsenic and thermal waters. There is a correlation between arsenic concentration and volcanic terranes.

ACKNOWLEDGEMENTS

I would like to take the opportunity to thank Gregory P. Miller for coming up with the idea of making a shoe-box sized arsenic speciation kit and garnering funding from EPRI and WERC for the necessary research. Thanks go out to Lynn Branvold, Senior Chemist at the Bureau of Mines and her staff, Barbara Popp and Terry Thomas, who taught me how to use the instruments needed, and also analyzed several samples.

The list of people and companies to thank for access to wells and springs is long. In no particular order, thanks to: Chris & Lawrence Hefner, George & Marge Austin, the City of Socorro, New Mexico Tech, the Bosque del Apache, ranch managers Steve Dobrott and Tom Waddel at the Ladder and Armanderis Ranches, Charles Motel, Artesian Bathhouse, Riverbend, Marshall Springs, and Jemez Springs. Thank you to my field assistants: Vladimir Ispolatov, Emily Kyle, Stephanie Maes, Stephanie and Karl Frisch.

Special thanks to the members of my committee, Dr. David I. Norman, Dr. Nelia W. Dunbar, and Dr. Robert S. Bowman, who each read several drafts of my thesis and had constructive criticism every time.

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INTRODUCTION

On October 31, 2001, the United States Environmental Protection Agency (EPA) reduced the Maximum Contamination Level (MCL) for arsenic in drinking water from 50 μg/l to 10 μg/l (EPA, 2001a). This decision is based on cost and health considerations and will become enforceable in January, 2006.

The cumulative toxicity of arsenic has only recently been recognized by epidemiologists. Chronic arsenic ingestion in Bangladesh, mainly through drinking arsenic-bearing groundwater, is described by the New York Times as "the greatest mass-poisoning in history" (Chowdhury, 1999). In the United States, we derive much of our drinking water from groundwater. In New Mexico, groundwater may provide as much as 90% of drinking water (Bitner et al., 2001), and in many areas of New Mexico, groundwater contains more than 10 μg/l arsenic. Costs of bringing New Mexico water into compliance of the new EPA standard range from $374 million to $436 million in capital costs, with operational and maintenance costs ranging between $16 million to $21 million per year (Bitner et al., 2001).

Arsenic occurs in many forms in natural waters. The most common forms of arsenic in groundwater are arsenite (As(III)), and arsenate (As(V)). Surface waters can contain organic arsenic species such as monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA). Species-specific removal techniques are used to minimize remediation costs. No EPA method exists to determine species, and current analytical

techniques are not capable of differentiating between species. Therefore, arsenic is reported as total dissolved arsenic.

This study fills a research gap in separating As(III), As(V), MMA, and DMA, and measuring their concentrations. This study developed two methods of separating aqueous arsenic species. The first method is a two-species method that separates As(III) from As(V). The evolution of the method is shown, including trial and error, quantification, and qualification methods for arsenic species, arsenic abundance, and analytical error. The second method is a four-species method that separates As(III), As(V), MMA, and DMA quantitatively. This study provides the framework for further research into developing a four-species arsenic separation method.

This study tests the developed two-species method on natural waters in the field. The results are used to gain insight into occurrences of total arsenic and As(III)/As(V) ratios in New Mexico water. Four field areas are chosen for investigation in this study: the Jemez Mountains geothermal area, Socorro geothermal area, Bosque del Apache National Wildlife Refuge, and the Truth or Consequences geothermal area. Areas of thermal waters were specifically chosen for this study because arsenic levels and As(III)/As(V) ratios in geothermal waters are typically high (Onishi, 1955). The measured arsenic concentrations are compared with previously published water quality data and related to regional geology. The differences in groundwater arsenic concentrations and the relationships between water chemistry and arsenic concentration are analyzed. Further, the relationship of arsenic concentration and speciation to bedrock aquifer type and geologic structures, are investigated.

BACKGROUND AND PREVIOUS WORK

Variability of Arsenic in the Environment

Arsenic Concentrations in Rocks

Arsenic is a naturally occurring metalloid, ranking 20th in crustal abundance of elements (Faure, 1998). Arsenic abundances in crustal rock average 2 ppm with elevated concentrations in shales (average of 13 ppm), clays (average of 13 ppm), and coals (Faure, 1998; Eaton et al., 1998). Onishi (1969) reports that volcanic glass and rhyolitic rocks are higher in arsenic than common rock types, with concentrations ranging from 2.0 to 12.2 with an average of 5.9, and 0.7 to 7.5 with an average of 3.5 ppm, respectively. Boyle and Jonasson (1973) report that arsenic concentrations for igneous rocks range from 0.18 to 113 ppm, with an average of 1.5 ppm for ultrabasic rocks, to 3.2 to 5.4 ppm, with an average of 4.3 ppm, for rhyolite. In sedimentary rocks, shales and argillites (average 14.5 ppm) contain the most arsenic (Boyle and Jonas son, 1973).

Elevated arsenic concentrations (>20 ppm in rock) accompany many economically important types of hydrothermal mineralization (e.g. Carlin-type, mesothermal, epithermal gold deposits, volcanogenic massive sulfide, Cu-porphyry). Therefore, arsenic is commonly used as a pathfinder element in geochemical exploration. Arsenic is greatly enriched in gold deposits of all types (Boyle and Jonas son, 1973),

where arsenic tends to be concentrated in minor, trace, and major amounts, either as separate arsenic minerals (e.g. arsenopyrite, realgar, orpiment) or as a minor or trace constituent in many sulfides, e.g. pyrite (Boyle and Jonasson, 1973).

Arsenic Concentrations in Water

Groundwater arsenic concentrations vary widely, but tend to range from < 2 µg/l to 100 µg/l (Focazio et al., 1999). Groundwater generally contains higher concentrations of arsenic than surface water (Onishi, 1969; Boyle and Jonasson, 1973). Stream, river, and lake waters contain an average of 1.7 µg/l arsenic, and groundwater concentrations average 17.9 µg/l (Boyle and Jonasson, 1973). The arsenic species expected in most natural waters is As(V) (Cullen and Reimer, 1989). Conversely, As(III) is the most common form of arsenic in hot springs, which reportedly contain the highest amounts of arsenic of all groundwaters (Onishi, 1969; Koch et al., 1999). Key points from several arsenic studies in hot springs are shown here to help illustrate the similarities and differences found in this study.

It has been known since the early 1970's that arsenic levels are high in hot springs and geysers of Yellowstone (Thompson, 1979). Arsenic concentrations range from < 7 µg/l to 1,700 µg/l. Subsurface reservoir water temperatures range between 164°C and 270°C. Although arsenic species are not investigated in this study, Thompson (1979) proposes that As(III) is surficially oxidizing to As(V) and precipitating with Fe(III). This results in a net arsenic decrease downstream from the geyser and hot spring sources. The author believes that the majority of arsenic issuing from the geysers and hot springs in Yellowstone National Park is As(III).

The Indonesian Ciwidey River is fed by an acid (pH < 1) hydrothermal crater lake (Sriwana et al., 1998). Arsenic concentrations in the crater lake averages 279 μg/l, arsenic in river water ranges from 0.3 to 3 μg/l, while soil samples range from 200 μg/l to 1,170,000 μg/l total arsenic (Sriwana et al., 1998). Arsenic correlates positively with chloride in water samples. Arsenic concentrations decrease downstream, and Sriwana et al. (1998) propose that As(V) is coprecipitating with Fe(III). Arsenic species are not investigated in this study, but the authors believe As(III) is present and oxidizing to As(V) *in situ*.

In the Meager Creek region of British Columbia, Canada, levels of arsenic are found to be elevated in hot springs (Koch et al., 1999). Arsenic concentrations in hot spring waters ranged from 237 μg/l to 303 μg/l with As(V) found as the dominant species. Nonthermal water in the region contains 5.4 μg/l arsenic. Koch et al. (1999) postulate that arsenic is leaching from rocks in the form of As(III) and oxidizing to As(V) before the water is issued in hot springs.

The Waikato River system, New Zealand, is part of the Broadlands-Ohaaki and Wairakei geothermal systems, one of the largest and best known geothermal areas in the world. Headwaters for the Waikato River are well above the geothermal system and have low arsenic levels (3 μg/l) that increase below the geothermal station at Wairakei to 121 μg/l (Robinson et al., 1995). Drainage water from the geothermal plant at Wairakei is 3,800 μg/l. The investigators determine that arsenic in the river is either of geothermal origin, naturally occurring, or from power plant effluent (Robinson et al., 1995). Arsenic(V) makes up 90% of the total arsenic most of the year, while As(III) dominates during the spring months when the cyanobacteria *Anabaena oscillaroides* reduces As(V)

to As(III) (Robinson et al., 1995). Arsenic in stream sediments and aquatic plants is measured, and the results show that sediments are the predominant arsenic sink. Arsenic increases with depth within the sediment cores (Robinson et al., 1995). No correlation to arsenic concentration in sediments is observed downstream; samples are taken over a stream reach of 300 km (Robinson et al., 1995).

In Hot Creek, California, Wilkie and Hering (1998) investigate As(III) and As(V) species issuing from a geothermal source; it is found that As(III) comprises approximately 32% of the total arsenic at the spring source, decreasing to 4% of the total arsenic downstream. Flow rate calculations imply a near complete oxidation of As(III) to As(V) in the course of one hour, an in-situ half-life for As(III) is 0.3 hours, while total arsenic concentration remains constant (Wilkie and Hering, 1998). The arsenic species are investigated using a modification of Ficklin's method, where As(V) is calculated taking the difference between the measured As(III) and the total arsenic concentrations (Wilkie and Hering, 1998).

It is consistently shown in these reviews that arsenic is high in hot springs with high reservoir temperatures (~200°C). Where species are investigated, either As(III) is the dominant species, or it is postulated that As(III) is present in the subsurface but either oxidized to As(V) soon before or after issuing to the surface. No organic arsenic species are found in the hot springs. Where total arsenic decreases downstream from the hot spring sources, the investigators postulate almost exclusively that As(V) is coprecipitating with Fe(III), resulting in a net loss of both elements from water.

Hot springs and cold springs in volcanic terranes contain the highest concentrations of arsenic in groundwater. Concentrations range from 0.2 to 40,000 μg/l

and 120 to 243,000 µg/l with averages of 2,090 µg/l and 22,200 µg/l, respectively (Boyle and Jonasson, 1973). This trend is consistent with the data available on specific hot springs enumerated here. The ratios of As(V)/(As(III)+As(V)) in fumarole waters range from 0.04 to 0.57 (Onishi, 1969). Thus, half or more of all the arsenic present in the measured fumaroles is As(III). Ballantyne and Moore (1988), report that arsenic can be positively correlated to temperature and chloride in geothermal systems. Ballantyne and Moore (1988) report that arsenic and chloride correlations cannot be used to indicate concentration or dilution because arsenic adsorbs to iron and alumina. A correlation of arsenic to chloride is shown in the Indonesian study (Sriwana et al., 1998), but no temperature correlation is observed in the Hot Creek study done by Wilkie and Hering (1998).

Levels of arsenic in groundwater are increased near arsenic-bearing mineral deposits and oilfield brines, e.g. Searles Lake, California, with 243,000 µg/l arsenic (Boyle and Jonasson, 1973). Levels of arsenic in groundwater range from 2 to 580 µg/l near the Bowena copper mine, a copper porphyry system on Bowen Island, British Columbia. Arsenic is associated with mineralized veins, porphyry dykes, and arsenopyrite-quartz veinlets (Boyle et al., 1998). The authors find that arsenic correlates negatively with calcium and positively with sodium (Boyle et al., 1998).

The majority of arsenic in seawater is in the form of As(V). The average ratios of As(V)/(total arsenic) in seawater at three different ocean sampling areas representing 14 sampling points are reported as 88%, 76%, and 86% (Onishi, 1969).

Anthropogenic Arsenic Contamination

Estimates comparing anthropogenic to natural arsenic input suggest that natural mechanisms contribute 60% of all arsenic in the environment (Cullen and Reimer, 1989). Most anthropogenic input of arsenic into the environment is due to smelting and coal combustion (Cullen and Reimer, 1989). Telephone poles in the United States are treated with copper-chromium-arsenate (CCA) to prevent decay and to deter termites and other insects from attacking the wood (Azcue, 1994, Origen Biomecial, 2001). Arsenic is released from the CCA-treated wood when the wood is burned or destroyed by mechanical abrasion or acid (e.g. acid rain). Arsenic compounds have historically been sprayed in the United States as insecticides, and arsenic has been used as a component in herbicides. Arsenic is used in livestock dips where cows and sheep are coated with arsenic compounds to kill pests. Historically, arsenic has been used in glues, pigments, glass, linoleum, herbicides, fungicides, fabrics, Venetian blinds, carpets, butcher paper, and medicine. (Azcue, 1994). The semi-conductor industry is the largest consumer of arsenic (Azcue, 1994). Gallium-arsenide chips compete with silicon products in the electronics industry because they are faster, but silicon components are cheaper. Gallium arsenide is used in LED's (light emitting diodes), IR (infrared) emitters, solar cells, laser windows, and tunnel diodes. Indium arsenide has been used in IR devices and experimental lasers (Azcue, 1994). At these levels, arsenic may be considered a minor point-source contaminant.

Arsenic Toxicity

High doses of arsenic are fatal, it has been used as the poison of choice for centuries for homicidal and suicidal uses (Azcue, 1994; Boyle et al., 1998). The adverse health effects of chronic low-level arsenic ingestion are strongly debated (e.g. Frost, 2000; National Research Council, 1999; Cullen and Reimer, 1989). It is generally agreed that As(III) is more toxic than As(V), and both of those inorganic species are more toxic than MMA or DMA. The lethal arsenic dose for 50% of a population (LD_{50}) is species-dependent. Diarsenic trioxide (As(III)), has an LD_{50} of 1.43 mg/kg body weight, arsenic acid, As(V), has an LD_{50} of 8 mg/kg body weight for As(V), and sodium cacodylate, DMA, has an LD_{50} of between 500 and 5000 mg/kg (EPA, 2001b). Chronic ingestion of high levels of arsenic in drinking water has been shown to cause arsenicosis (World Health Organization, 2001). Diagnostic symptoms include hyperkeratosis, which manifests itself as nodular lesions on the palms of the hands and bottoms of feet, and hyperpigmentation, which is seen as finely freckled patterns of pigmentation and depigmentation on the trunk and extremities of the body. Skin cancers are commonly associated with chronic arsenic poisoning, as are filter organ cancers e.g. bladder, liver, stomach, and kidney cancer (World Health Organization, 2001). In Taiwan and Bangladesh, concentrations of arsenic in drinking water locally exceed 1000 μg/l (Chen et al., 1994; Chowdhury, 1999; World Health Organization, 2001). As a consequence, more than 50 million people in Taiwan, Bangladesh and West Bengal, India, currently are suffering from arsenic related illnesses (Chen et al., 1994; World Health Organization, 2001).

Arsenic Geochemistry

Arsenic can occur in four aqueous oxidation states (+5, +3, 0, and -3), but it generally occurs in the pentavalent (As(V)) or trivalent (As(III)) states (Onishi and Sandell, 1955). Arsenic is classified by its valence state (e.g. oxidation state) and by whether or not it is an organic compound (contains carbon in the molecule). Arsenic travels as the oxyanions As(III) and As(V) in ground- and surface water. The ionic charge is governed by the pKa's (negative log of the dissociation constant). A distribution diagram of arsenic ions as a function of pH is shown in Fig. 2.1. This diagram can be used to determine what species of arsenic are thermodynamically predominant at standard temperature and pressure.

The pKa's for As(III) are 9.23, 12.13, and 13.4 (National Research Council, 1999). At pH < 9.23 (see Fig. 2.1a), As(III) is found as the neutral H_3AsO_3 molecule. As a neutral molecule, As(III) has little affinity for either anion or cation exchange resins. At a pH of >9.23, the dominant form of As(III) is $H_2AsO_3^-$.

The reaction rate for the oxidation of As(III) to As(V) is poorly known. A review article by Volke and Merkel (1999) summarizes oxidation rates ranging from complete oxidation in hours to weeks, depending on conditions. Various researchers have attempted to slow As(III) oxidation by adding ascorbic acid, nitric acid, or freezing the samples. No method has been shown to reliably maintain the species for long periods of time. Conditions that appear to accelerate the chemical oxidation of As(III) to As(V) include exposure to the catalyst sunlight, oxygen, ozone, chloride, and peroxide.

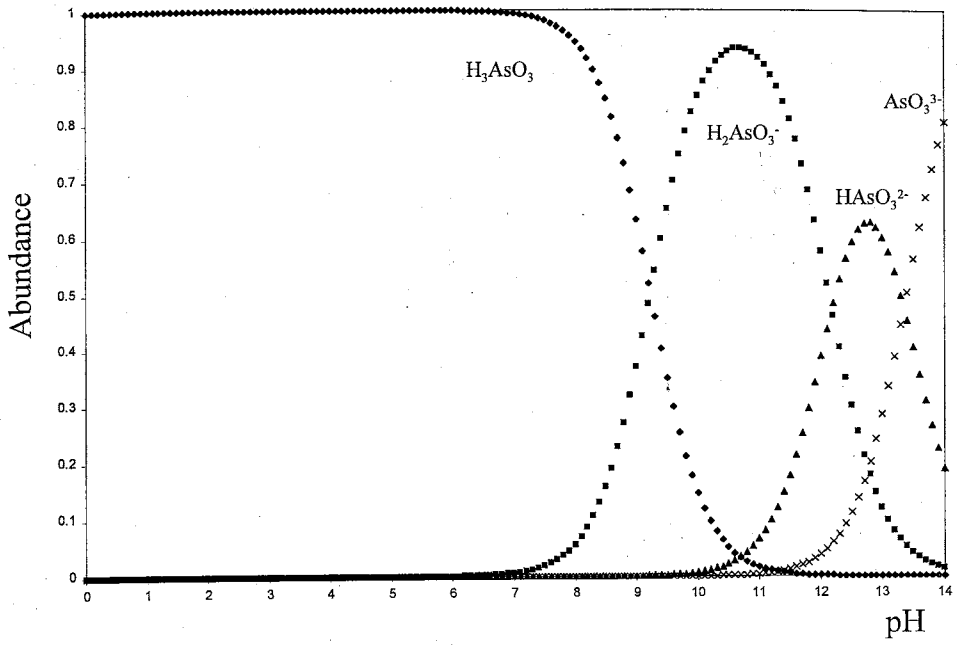


Figure 2.1a. Percent distribution diagram of As(III) as a function of pH at STP.

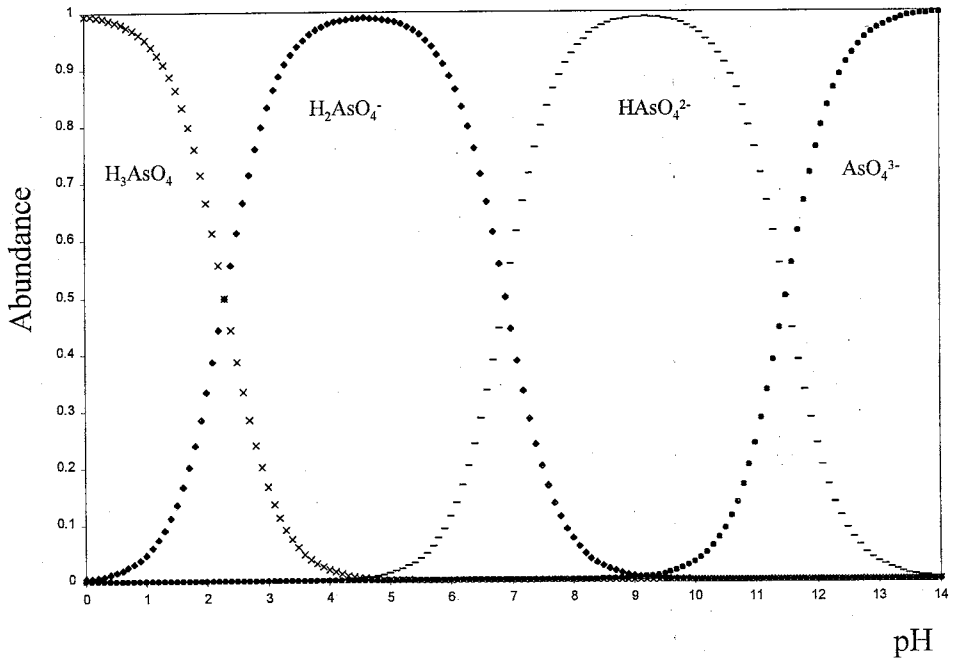


Figure 2.1b. Percent distribution diagram of As(V) as a function of pH at STP.

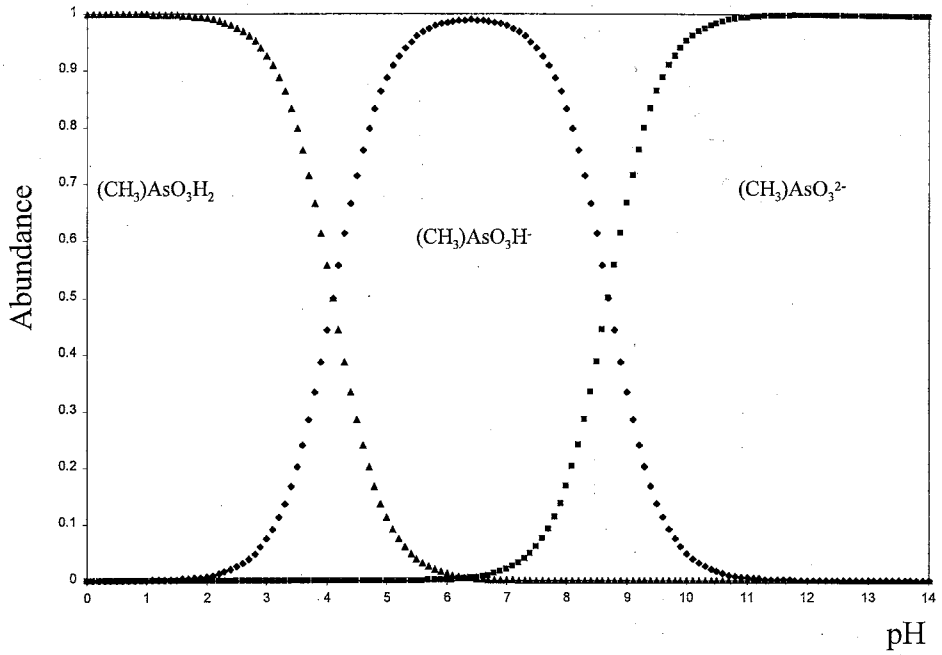


Figure 2.1c. Percent abundance diagram of MMA as a function of pH at STP.

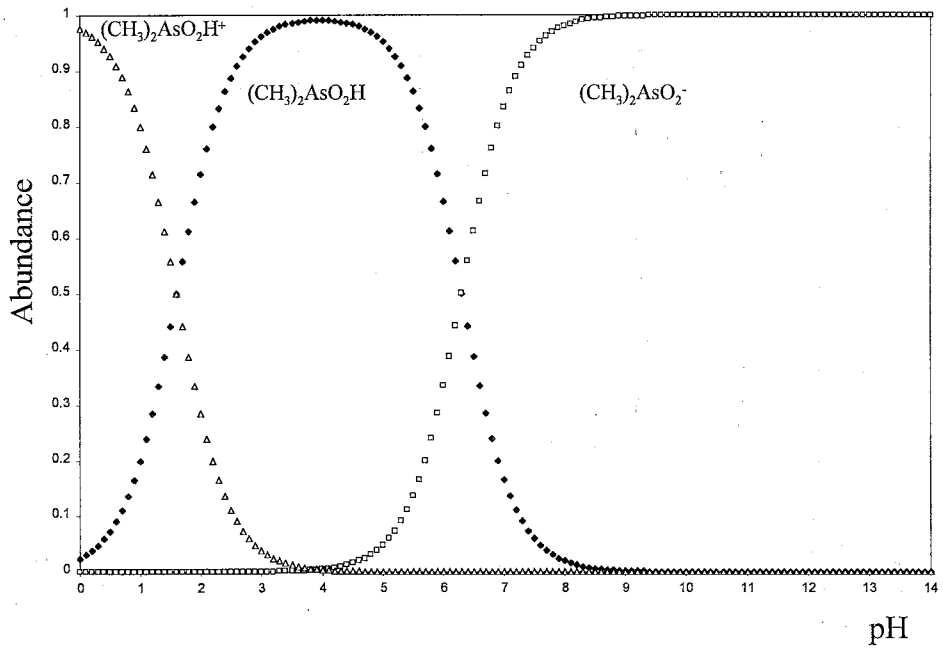


Figure 2.1d. Percent abundance diagram of DMA as a function of pH at STP.

Effects of temperature, concentration, and surface area have not been investigated (Volke and Merkel 1999).

The pKa's for As(V) are 2.3, 6.9, and 11.5 (see Fig. 2.1b). The dominant ion for As(V) at pH > 2.3 is an anion; thus, As(V) is an anion in most groundwaters. The arsenate oxyanion has a strong affinity for anion exchange and will readily sorb to anion resins. The removal of As(V) from an anion resin requires the exchange of an anion that has a greater affinity for the resin than does As(V), or the neutralization of the charge by lowering the pH to <2.3. Chloride ions have very strong affinities for anion exchange resin and hydrochloric acid (HCl) has a very low pH (a 10% solution of HCl has a pH of 0.92). Both the pH and resin affinity make HCl good for stripping As(V) from anion resins.

Mobility of inorganic arsenic is thus mainly dependent on the species. The interconversion between As(III) and As(V) is Eh-dependant and it has been proposed by Cherry et al. (1979) that arsenic can be used as a redox indicator in groundwater. Low Eh conditions (below -0.3 to -0.5 mV, e.g. bog waters) can reduce As(V) to As(III). If As(V) is reduced in lakes, swamps, or bogs, the site can become a point source for arsenic contamination in groundwater. In surface waters, there are two transport mechanisms for As(V): the reduction of As(V) to As(III) can mobilize arsenic sorbed on clays or Fe/Mg oxides, and As(V) can be mobilized in colloidal transport (e.g. as a suspended solid in surface waters) (National Resource Council, 1999; Cullen and Reimer, 1989).

Naturally occurring organic arsenic is rarely detected in groundwater, however, concentrations of organic arsenic in surface waters up to 10% of total arsenic are documented (Marshall and Fairbridge, 1999; Cullen and Reimer, 1989), while others

have documented concentrations as high as 25% (Brockbank et al., 1988). Inorganic arsenic salts are microbially methylated in soils and surface waters, where they can be taken up in the food chain (Cullen and Reimer, 1989). Higher-level organisms (including humans) also methylate inorganic arsenic salts and excrete arsenic in sweat, urine, and breast-milk. Organic arsenic contamination is generally linked to point source contamination of soil by organic herbicides and fungicides (Eaton et al., 1998; Azcue, 1984).

The pKa's for the organic species MMA are 4.1 and 8.7, indicating that MMA is found as an anion in pH's > 4.1. In solutions of pH < 4.1, MMA is a neutral molecule with a weak dipole due to the $\delta+$ on the methyl group. This weak dipole allows MMA to be weakly retained on exchange resins. The organic species DMA has pKa's of 1.6 and 6.3; the chemical ion that dominates below pH 1.6 is a cation (DMA^+), with the neutral ion dominating between pH 1.6 and 6.3. This neutral ion has a dipole due to a $\delta+$ on the methyl groups. At pH above 6.3, DMA has a negative charge. In acidified samples, DMA is a cation, and has a strong affinity for cation resin.

United States Arsenic Regulations in Drinking Water

The presence of arsenic in drinking water has been a growing concern worldwide. In 1996, an amendment to the Safe Drinking Water Act required the Environmental Protection Agency (EPA) to lower the maximum contaminant level (MCL) of arsenic in drinking water by January 1, 2000. The MCL was set at 50 µg/L (50 ppb) in 1975, based on a standard originally established by the Public Health Service in 1942. In March 1999,

the National Academy of Sciences (NAS) recommended that the EPA lower the standard as soon as possible, without suggesting a specific MCL. The EPA did not meet its January 1, 2000, mandate to establish a new MCL for arsenic in drinking water. Just several months later, however, on May 24, 2000, the EPA announced a new MCL of 5 µg/l, an order of magnitude lower than the old standard (EPA, 2001c). This new standard has caused an uproar among municipalities throughout the United States. It also prompted researchers to look further into arsenic chemistry and geochemistry in order to improve the understanding of distribution of arsenic and, ultimately, to design more effective remediation methods. On January 22, 2001, the EPA declared a 10 µg/l enforceable standard for implementation in three years. On March 20, 2001, President Bush reversed the EPA MCL back to 50 µg/l. On July 27, 2001, the House of Representatives voted to reinstate the new 10 µg/l arsenic standard. On August 2, 2001, the U.S. Senate voted 97 to 1 in favor of the 10 µg/l arsenic standard. On Halloween, 2001, the EPA announced its final rule of 10 µg/l, enforceable beginning January 2006 (EPA, 2001a).

Implications of the New MCL and Remediation Techniques for Arsenic

It is estimated nationwide that 13.6% of all drinking water municipalities will be affected by the MCL proposed by the EPA and will have to remediate their water before supplying it to the public. Building costs for these facilities are estimated to be over $6 billion in the USA. New Mexico has the 6th highest median arsenic value for all states in the United States (Focazio et al., 1999). Remediation will become an important concern

for many New Mexico municipalities. Startup costs for an experimental arsenic treatment plant to remediate one well that doesn't meet the 50 μg/l standard are estimated at $4.1 million. Operation expenses are expected to be a total of $273,000 annually (Bernalillo County Environmental Health Department, 2000). There are several methods of removing arsenic from water. If arsenic is present as As(III), it must be oxidized to As(V) before removal. If As(V) is present, no pre-treatment is necessary. Generally, As(V) is removed using activated alumina (aluminum hydroxide gel) or ferric iron (Golden, 2000; Driehaus, 2000; Jekel and Seith, 2000).

The method developed in this study for speciating arsenic has commercial applications for municipalities whose waters will need to be remediated under the new MCL. If As(III) is dominant, preoxidation is necessary for remediation. If As(V) is dominant, no preoxidation is required. Thus, remediation techniques are species specific to minimize costs. No commercial method for speciating arsenic is currently available (National Research Council, 1999), and methods that have been proposed by other researchers (e.g. Ficklin, 1983; Grabinski, 1981) are shown in this study to be flawed. Should the EPA take a species-based approach to setting the MCL for arsenic, then the method developed here will show what species are present. This is currently not being proposed (EPA, 2001c). EPA drinking and wastewater arsenic methods describe methods for the analysis of total arsenic (EPA, 2001c). No EPA drinking or wastewater method describes measuring individual arsenic species.

Previous Speciation Methods

Overview of Speciation Techniques

Several methods that have been proposed for speciating arsenic follow:

a) Soil and biomass laboratory extractions (Bermond et al., 1998; Yamamoto, 1975);

b) Measuring arsenic before and after reduction using hydride-generation detection (Hasegawa et al., 1994; Yamamoto, 1975);

c) Column chromatography coupled with atomic absorption detection (Iverson et al., 1979);

d) Ion exchange separation for later analysis (Grabinski, 1981; Ficklin, 1983; Meng and Wang, in press);

e) partial ion exchange separation and calculation of species by difference (Wilkie and Hering, 1998; Clifford and Ghurye, 2000).

Two-Species Arsenic Separation Method by Ion Exchange

The method used by Ficklin (1983) to separate As(III) from As(V) forms the starting point for the investigation described in this text. This method separates As(III) and As(V). For this method, approximately 2.3 grams of BioRad 100-200 mesh X8 chloride exchange resin are slurried to just below the top of a BioRad glass econo-column with dimensions of 7 mm diameter and 10 cm height (Ficklin, 1983). A 5-ml arsenic species standard is acidified with 0.5 ml HCl, creating a 0.12 M HCl solution that has a pH of 0.92. This solution is then introduced into the column. The eluent, a 10% HCl solution, is introduced in 5 ml aliquots in the field; laboratory procedure is not described

(Ficklin 1983). Samples are taken in 1 ml aliquots for laboratory standard tests and in 5 ml aliquots in field collection (Ficklin, 1983). Flow rate is not addressed, but it is stated that a separation takes approximately 15 minutes in the field (Ficklin, 1983). The first species to elute from the column is As(III), which elutes between 0 and 10 ml. The second species to elute from the column is As(V), which elutes between 10 and 20 ml (Ficklin, 1983). The behavior of organic species is not reported for this methodology.

Four-Species Arsenic Separation Method by Ion Exchange

The four species method that we started our research from is described by Grabinski (1981) and will hereafter be referred to as ASK4, which stands for Arsenic Speciation Kit for Four species. This method uses cation and anion exchange resin to separate As(III), As(V), DMA, and MMA. BioRad AG 1-X8 100-200 mesh anion exchange resin is slurry packed to a height of 9 cm in a 35-cm tall by 1-cm diameter glass tube that is equipped with a 100-ml reservoir and adjustable N_2 gas pressure (Grabinski 1981). Flow rate is 5-10 ml/minute. BioRad AG 50 W-X8 cation exchange resin is slurried on top of the anion column to a height of 26 cm, resulting in a 35 cm tall column (Grabinski, 1981). A 2-ml arsenic sample is introduced into the column, eluted with 55 ml 0.006 M trichloroacetic acid (TCA), 8 ml 0.2 M TCA, 55 ml 1.5 M NH_4OH, and 50 ml 0.2 M TCA. As(III) elutes in the first 23 ml, followed by MMA, which elutes from 26 to 55 ml. As(V) elutes from 65 to 85 ml, and DMA elutes from ~125 to 155 ml (Grabinski, 1981). Samples are collected in known volumes that range from 3 to 20 ml. It should be noted here that the arsenic standard concentrations that Grabinski is working with are very high, ranging from 310, 2576, 620, and 330 µg/l for As(III), MMA, As(V),

and DMA, respectively (Grabinski,1981). The detection limit is stated at 10 μg/l per species, due to the dilution of the input concentration by the eluent.

Overview of Study Areas for Field Testing

Field Site Selection Criteria

As mentioned earlier, arsenic levels are higher in thermal than in nonthermal groundwater. In hot springs, As(III) is the dominant species, but it tends to be oxidized to As(V) during discharge and/or in transport of surface water. Overall high arsenic concentrations and variable As(III)/As(V) make geothermal areas particularly appropriate for the studies of arsenic speciation. Therefore, four regions in New Mexico (Fig. 2.2) that have known geothermal activity and high arsenic concentrations are chosen. Of the 47 sites that are sampled, 27 are thermal and 20 nonthermal. Twenty-six are springs, 20 are wells, and one is a shallow lake. Site numbers are used on all figures to represent locations.

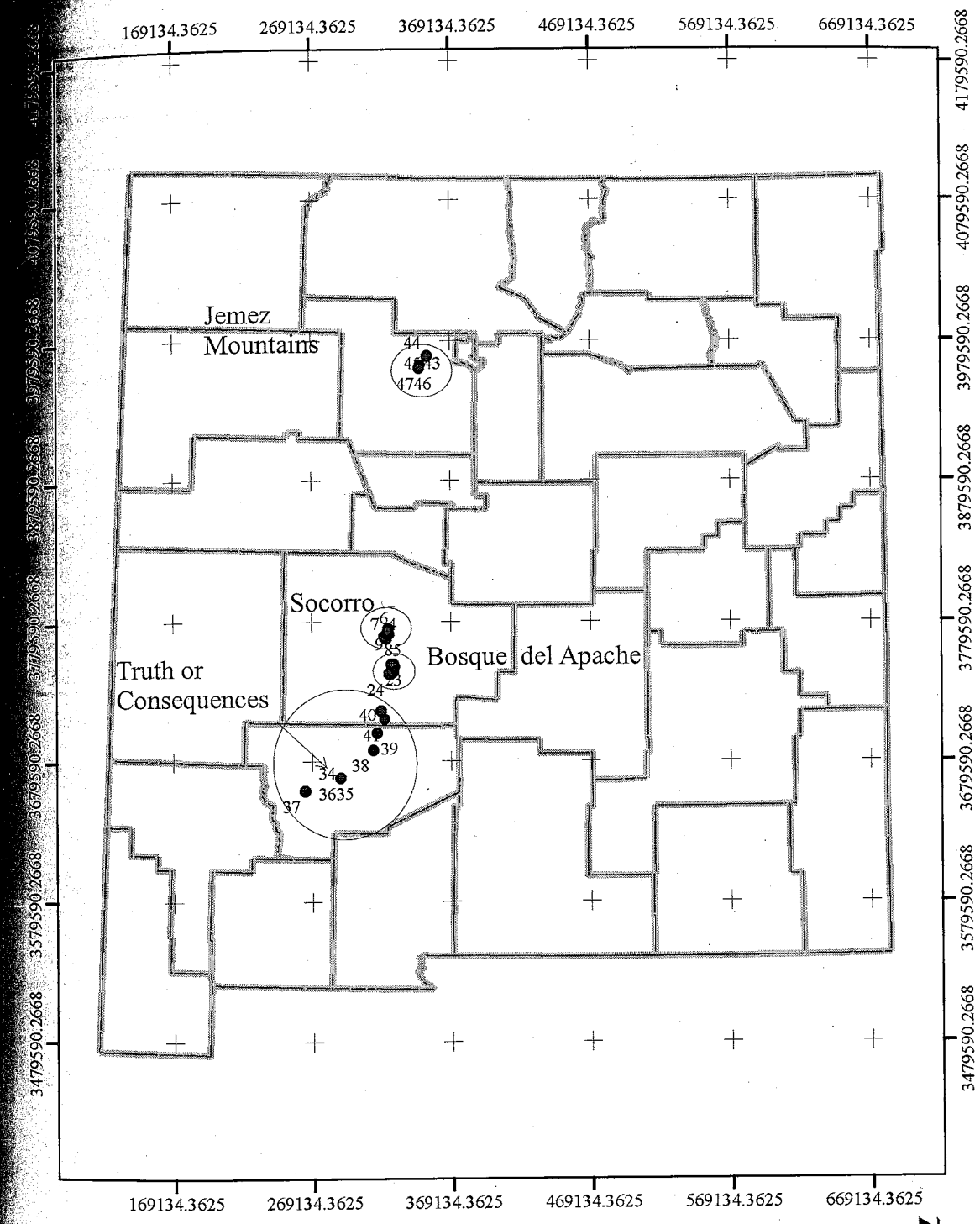


Figure 2.2 Map of New Mexico Showing Sample Regions.

Table 2.1. Field Site Legend.

Site	Sample Site	Site Location	Site	Sample Site	Site Location
1	Socorro Springs	Socorro	25	Riverbend Well	Truth or Consequences
2	Sedillo Springs	Socorro	26	Indian Springs Well	Truth or Consequences
3	Eagle Picher Well	Socorro	27	Geronimo Springs	Truth or Consequences
4	Industrial Well	Socorro	28	Charles Motel Well	Truth or Consequences
5	School of Mines	Socorro	29	Marshall #4 Spring	Truth or Consequences
6	Olson Well	Socorro	30	Marshall #5 Spring	Truth or Consequences
7	Cook Spring	Socorro	31	Marshall #2 Spring	Truth or Consequences
8	Austin Well	Socorro	32	Marshall #3 Spring	Truth or Consequences
9	Intor Well	Socorro	33	Marshall #1 Spring	Truth or Consequences
10	Bushman Well	Socorro	34	Marshall DW Spring	Truth or Consequences
11	Holmes Well	Socorro	35	Artesian Well	Truth or Consequences
12	Lattman Well	Socorro	36	Hay-Oh-Kay Well	Truth or Consequences
13	Hefner Lake	Socorro	37	Los Animas Spring	Truth or Consequences
14	Thermal Well	Bosque del Apache	38	Deep Well	Truth or Consequences
15	17A Well	Bosque del Apache	39	Hard Luck Crossing	Truth or Consequences
16	HQ Well	Bosque del Apache	40	Antelope	Truth or Consequences
17	12A Well	Bosque del Apache	41	Hackberry Well	Truth or Consequences
18	13B Well	Bosque del Apache	42	Grotto Spring	Jemez Mountains
19	1NE Well	Bosque del Apache	43	Soda Dam main spring	Jemez Mountains
20	9NW Well	Bosque del Apache	44	Spence Upper Spring	Jemez Mountains
21	9NE Well	Bosque del Apache	45	Spence Lower Spring	Jemez Mountains
22	1NW Well	Bosque del Apache	46	Travertine Mound Spring	Jemez Mountains
23	3N Well	Bosque del Apache	47	Gazebo Spring	Jemez Mountains
24	DW Well	Bosque del Apache			

Jemez Mountains Geothermal Field

The Valles Caldera hosts the Jemez Mountains geothermal field, a high-temperature system in northern New Mexico. The caldera is east of the Colorado Plateau, near its junction with the western margin of the Rio Grande rift zone. The Jemez Mountains region is a young volcanic field created by two massive caldera-forming events. The catastrophic eruptions formed the Bandelier Tuff, that comprises two major members: the Otowi Member (1.61 Ma) and the Tshirege Member (1.22 Ma) (Nowell,1996). 1996). The Valles Caldera is marked by dozens of thermal springs.

The six sample sites include a) Spence Springs upper (No. 44), b) Spence Spring lower (No. 45), c) Grotto Spring (No. 42), d) Soda Dam Main Spring (43), e) Gazebo (No. 47), and f) Travertine Mound (No. 46)(Fig. 2.3).

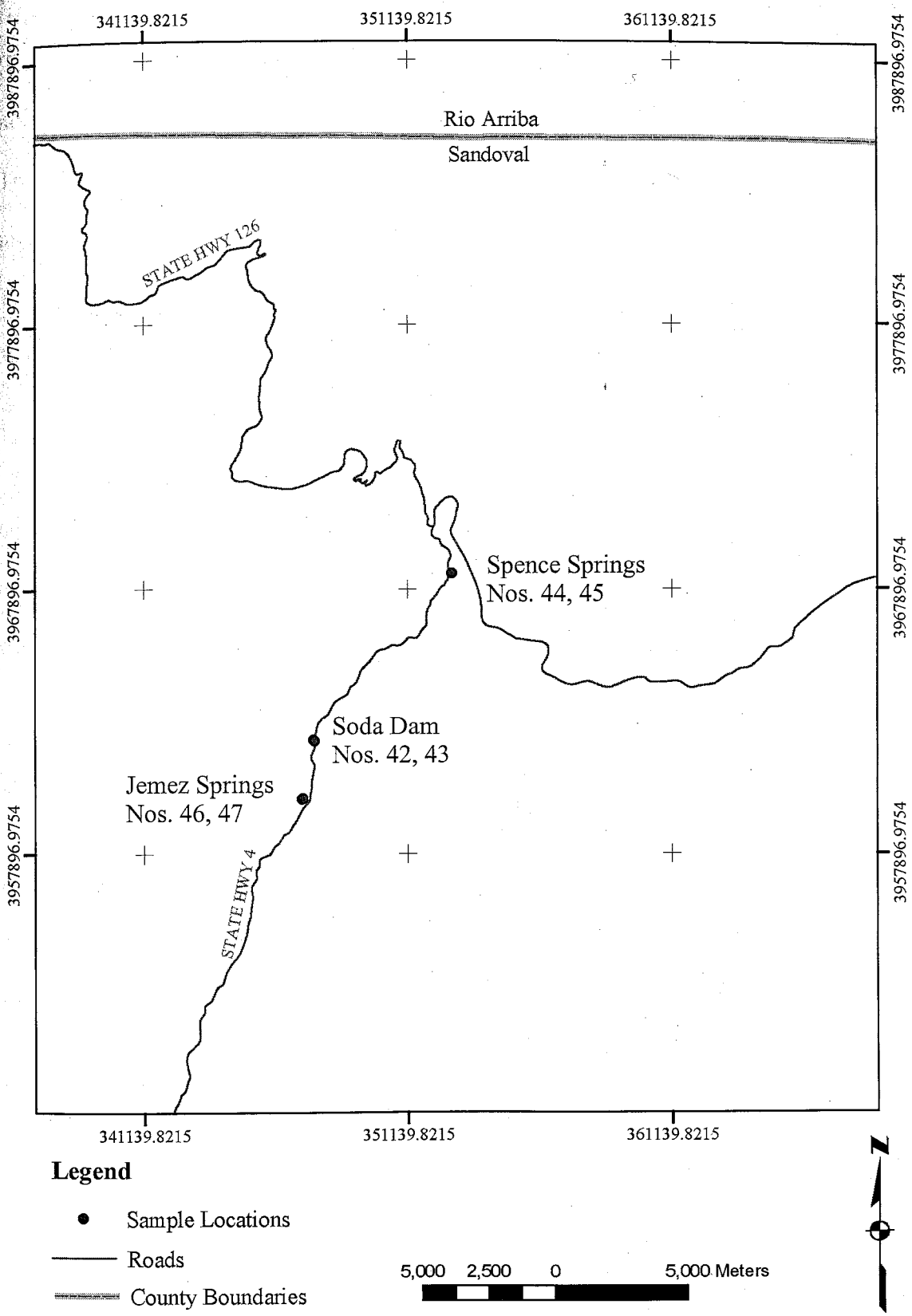


Figure 2.3 Map of the Jemez Mountains Showing Sample Locations.

A ^{36}Cl study investigates meteoric recharge and fluid flow in the Jemez caldera (Rao et al., 1996). Meteoric waters seep to depths of several kilometers along the northern boundary of the Valles Caldera ring fracture system and migrate southward. They are heated and forced upward along major caldera faults, where they mix with local meteoric water and discharge in hot springs or unplugged anthropogenic drillholes. The Travertine Mound, Gazebo, and two springs at Soda Dam ("Main" and "Grotto") are Jemez Fault zone hot springs. The Jemez Fault zone trends northeast, perpendicular to the caldera dome boundary (Fig. 2.4.)

Kelly and Reinert (1996) studied arsenic stratification in the Santa Fe Formation. Groundwaters are collected from wells along the drainages of the Jemez River and Rio Salado. They measured high concentrations of arsenic in groundwater in the Santa Fe Formation, believed to be caused by volcanic activity in the Valles caldera. The samples are taken at various depths during the drilling of drinking water wells. The author concludes that pumping a well caused arsenic levels in groundwater samples to increase. Arsenic concentrations ranged from 21 μg/l to 58 μg/l. Arsenic levels increased with pumping for all wells in the study area. Samples are not filtered because municipal water in that region is unfiltered. Thus, arsenic values represent concentrations that are present in the drinking water. The results show that arsenic concentration generally increased with depth (from 9 μg/l to 29 μg/l), but there are also stratigraphically controlled compartments with water that contained lower (<5 to 12 μg/l) arsenic concentrations (Kelly and Reinert, 1996).

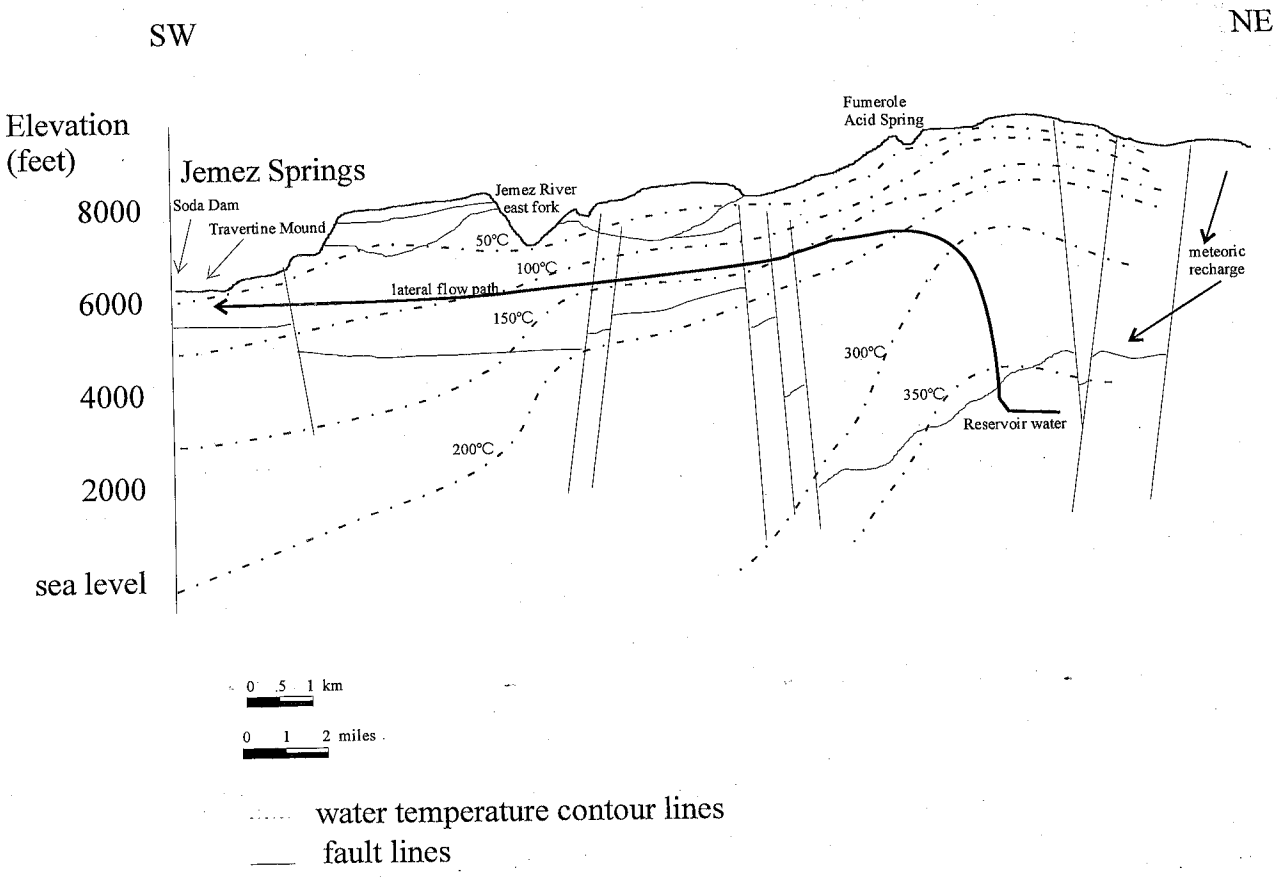


Figure 2.4. Jemez Mountains Geothermal Region: Cross-section after Rogers et al. 1996.

Socorro Region

Thirteen sites in the Socorro region are sampled (Fig. 2.5). Of the 13, Socorro Springs (No. 1), Sedillo Springs (No. 2), and Cook Spring (No. 7) are thermal springs. Nine nonthermal samples are taken, including Lattman well (No. 12), Bushman well (No. 10), Holmes well (No. 11), Olson well (No. 6), School of Mines well (No. 5), Industrial well (No. 4), Eagle Pitcher well (No. 3), Dr. Austin's well (No. 8), and the Intor company well (No. 9). A shallow (<4 feet deep) lake (Hefner Lake) (No. 13), formed when sand and gravels were quarried for highway construction, is also sampled. The Socorro geothermal area is located in central New Mexico within the Rio Grande rift valley, west of the Rio Grande River. The Socorro region lies in a north-south trending basin that is fault-controlled with syn-rift sediments overlying eastward dipping normal fault blocks at a depth of several thousand meters (Chapin, 1983; Mailloux et al., 1999). The region is bounded to the west by Socorro Peak, a caldera (33 Ma) horst block that was rotationally displaced in "domino style faulting" during an extensional event in the Tertiary (Chamberlin, 1983, Barroll, 1989; Mailloux et al., 1999). The rift faults are deep, high-angle normal faults formed during extension of the Rio Grande basin in the last 28 Ma (Mailloux et al., 1999). Socorro Peak was the location of small-scale mining activity when silver was discovered in 1867 (Lasky, 1932). Mining continued until the 1890's, when the silver price dropped. Minerals reported from Socorro Peak include malachite ($Cu_2(CO_3)(OH)_2$), fluorite (CaF_2), manganese oxides (psilomelane?), barite ($BaSO_4$), calcite ($CaCO_3$), galena (PbS), mimetite ($Pb_5(AsO_4)_3Cl$), vanadinite ($Pb_5(VO_4)_3Cl$), wulfenite ($PbMoO_4$) and argentite (Ag_2S) (Lasky, 1932). Silver values ranged from 2 to 7.5 oz/ton, while gold values ranged from 0.02 to 0.25 oz/ton (Lasky, 1932). The

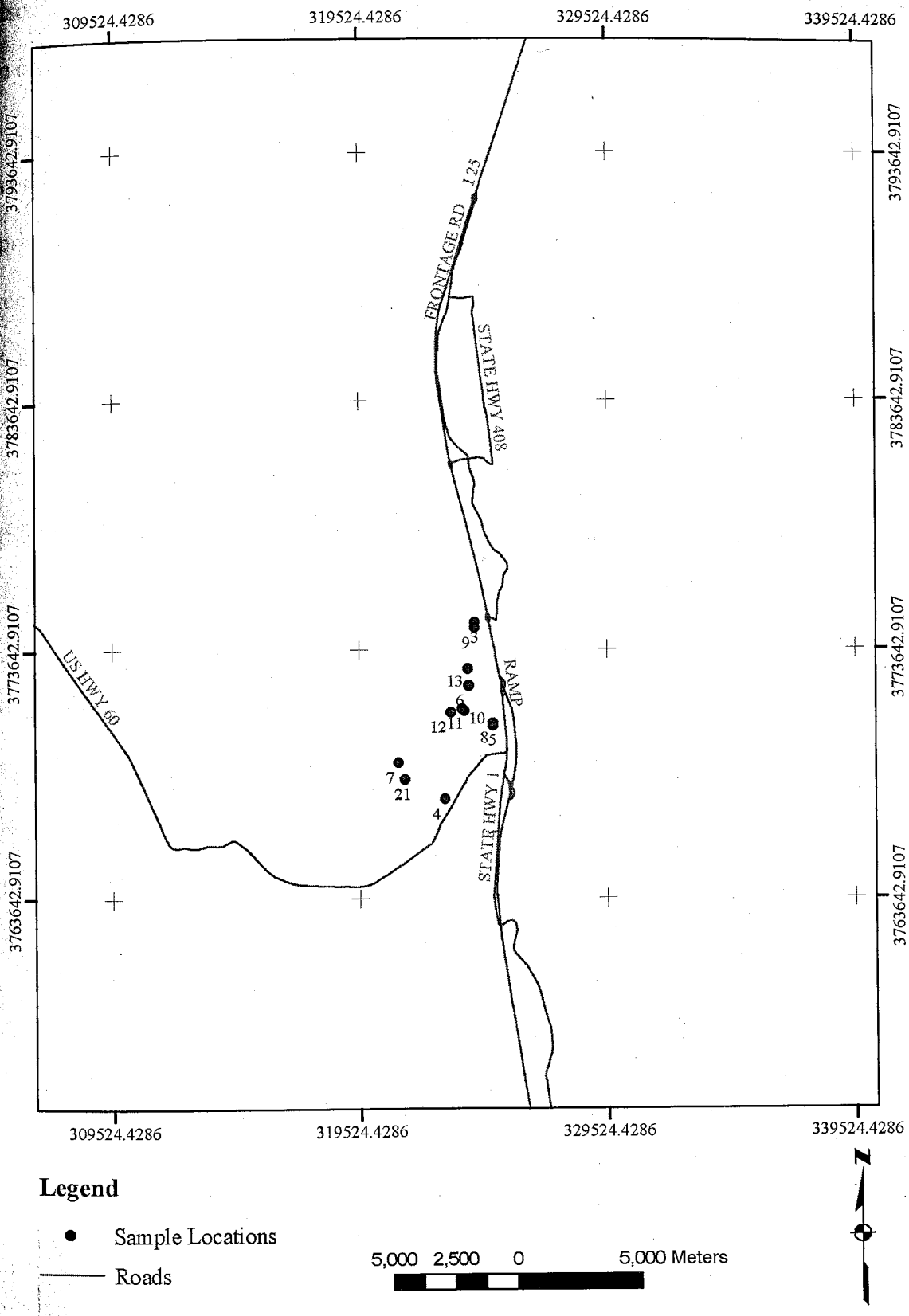


Figure 2.5 Map of the Socorro Region Showing Sample Locations.

discovery of mimetite in workings in Socorro Peak is important to this study, because it is an arsenic bearing mineral.

Groundwater flow and temperature anomalies in the Socorro thermal springs have been investigated by many researchers. It is generally accepted that deep recharge to the springs is from the Magdalena Mountains, while shallow recharge is local, from the Lemitar Mountains and Socorro Peak (Barroll, 1989; Gross and Wilcox, 1993; Mailloux et al., 1999). Residence times for shallow, young, and local recharge water is on the order of four years (Gross and Wilcox, 1983). Residence times for the older water, coming from the Magdalena Mountains, is noted to be "substantially older than the half-life of tritium (12.3 years)" (Gross and Wilcox, 1983). The water recharging from the Magdalena Mountains makes up the majority of the recharge water for the three thermal springs in Socorro. There are two proposed paths of travel for this water: a shallow recharge path and a deep recharge path, where water is forced beneath the Popotosa Clay layer (Gross and Wilcox, 1983). A cross-section of this region, depicting groundwater flow patterns after Gross and Wilcox (1983) is shown in Fig. 2.6. There is some speculation by Anderholm (1983) that chloride-rich water discharging in the thermal springs is from upward flow of geothermal fluids along the fault zone or from upward flow of deep-basin groundwater. Contradicting this theory, Gross and Wilcox (1983) state that no hydrologic connection between reservoirs related to the geothermal anomaly and ground-water systems are observed and that all water in thermal springs are of meteoric origin. It is estimated by Mailloux et al. (1999) that the thermal anomalies of Socorro, Sedillo, and Cook springs are the result of Magdalena Mountain recharge water discharging through a 'hydrologic window' from a regionally extensive confining unit.

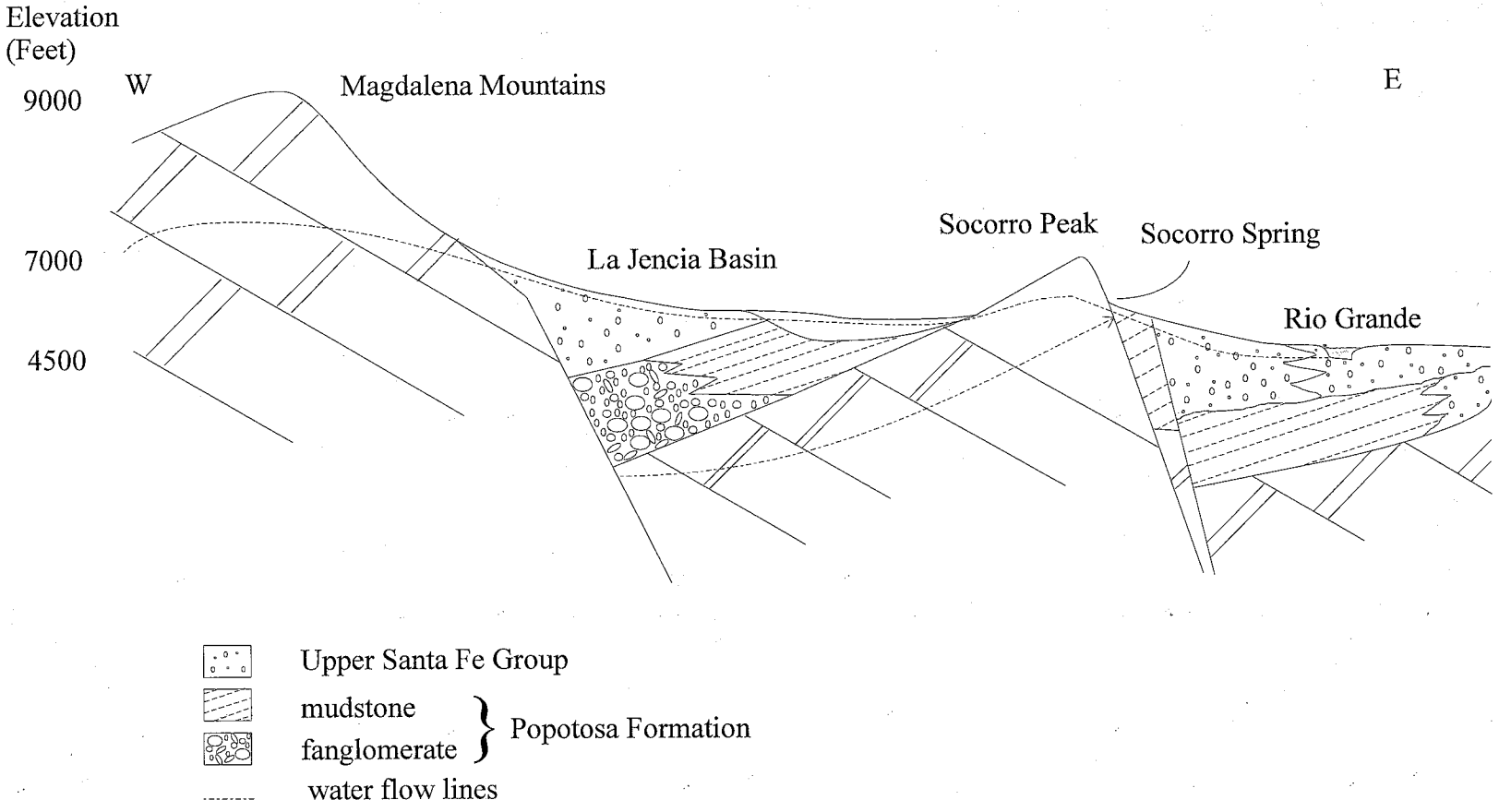


Figure 2.6. Cross-section of Socorro Geothermal Water Flow after Gross and Wilcox, 1983.

The thermal anomaly can be explained using a model that assumes that approximately 5% of the recharge water from the Magdalena mountains penetrates to a depth of 2.8 km below the sedimentary pile before issuing in the springs (Mailloux et al., 1999). Gross and Wilcox (1983) state that cation exchange (Na replacing Ca) occurs along a north-trending line in the Socorro Mountains in groundwater, and that this process is related to the geothermal anomaly of the Socorro Mountains. This is also observed by Anderholm (1983).

A mid-crustal magma body has been outlined in the Socorro region (Balch et al., 1997; Sanford, 1983; Sanford et al., 1983; Mitchell and Jiracek, 1983). The depth of the body is 19 km (± 0.5 km) based on a 30-year study of data by Balch et al. (1997). Sanford et al. (1983) state that magma movement is considered the primary source of crustal stress and earthquake swarms in this region. The focal depth ranges from 4 to 14 km; a sharp cutoff in number of hypocenters between 11.5 and 14 km indicates a ductile zone in the crust (Sanford, 1983). Mitchell and Jiracek (1983) have magnetotelluric (MT) and COCORP evidence that indicates that a magma lens is present from 20 to 25 km depth and that the rift basin has a depth of 4.5 km from the surface.

A 200 m thick surface layer is deemed to grossly represent the upper groundwater environment while highly saline groundwater is found at depths below the 200 m groundwater level to a depth of 4.5 km (Michell and Jiracek, 1983). A decrease in resistivity in the 10 to 25 km range is suggestive of high-pressure pore fluids trapped beneath an impermeable ductile cap, which is believed to be at 10 km (Michell and Jiracek, 1983). Fluids may be derived from "mineral dehydration at depth or from

ijected magma" (Michell and Jiracek, 1983). Water in this system circulates to depths of 2.8 km (Mailloux et al., 1999).

Bosque Del Apache

The Bosque del Apache National Wildlife Refuge (hereafter referred to as Bosque) is located in the Central Rio Grande Rift zone, approximately 15 miles to the south of Socorro (Fig. 2.7). This study area is chosen because the thermal well (No. 14) was previously thought to be "high" in arsenic (Barroll and Reiter, 1995), although this is not confirmed by later studies. Branvold (2001) reports that the thermal well has an arsenic concentration of 39 µg/l. Eleven irrigation wells are sampled, including the thermal well (No. 14) and 10 nonthermal wells (Nos. 15 to 23). The only source of potable water is from the drinking-water well (No. 24).

The thickness of Quaternary and Tertiary sand and gravels in this part of the rift could be greater than several thousand meters thick (Anderholm, 1983; Barroll and Reiter, 1995). The basin is bounded to the east by Paleozoic rocks and to the west by Tertiary volcanics, Paleozoic, and Precambrian rocks (Anderholm, 1983). The Rio Grande river flows through the Bosque. Groundwater flow is generally north to south, following the flow of the Rio Grande (Anderholm, 1983; Barroll and Reiter, 1995). The basin is part of the Socorro groundwater system, with recharge from the west consists of relatively fresh water, while recharge from the east consists of lower quality, high sulfate water (Barroll and Reiter, 1995). There is local groundwater recharge due to high volumes of water being used for irrigation of farmland and for flooding for ponds at the Bosque (Barroll and Reiter, 1995).

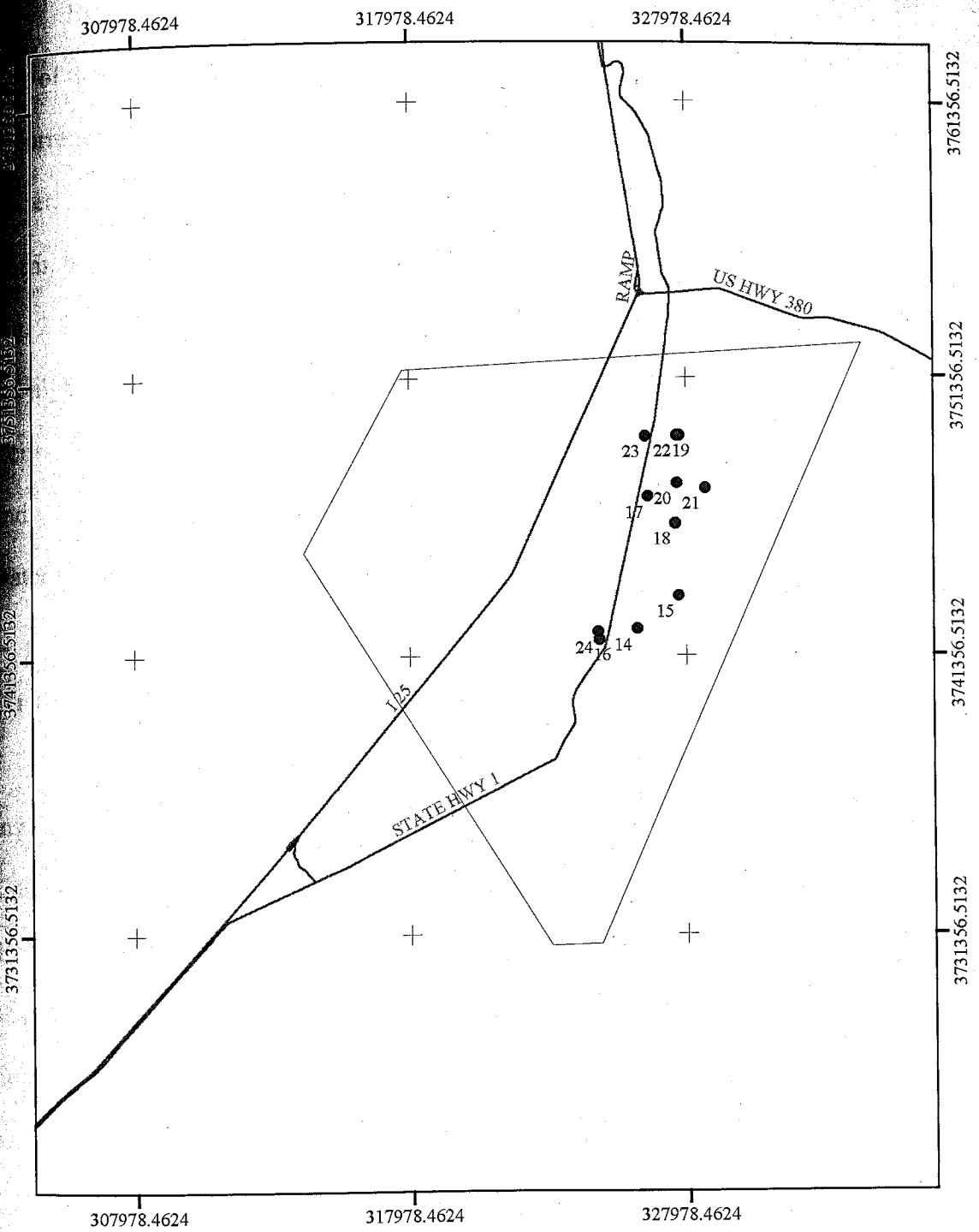


Figure 2.7 Map of the Bosque del Apache National Wildlife Refuge Area, Showing Sample Locations.

Barroll and Reiter (1995) correlate Bouguer gravity data and temperature well logs of three wells. They conclude that the thermal well intersects a high-angle fault. The occurrence of warm water at this well is deemed "a localized phenomenon" (Barroll and Reiter, 1995). They also propose that the north-south trending fault is a conduit for deep, warm, high TDS, high Cl water being pumped from the thermal well (see cross-section Fig. 2.8). Shallow basement rock forms an aquitard and forces warmer waters up along the high-angle fault. Local recharge is cool, low TDS, and low Cl water (Barroll and Reiter, 1995). It is suggested that deeper hydrothermal waters east of the thermal well, and west of the river, could be harnessed to keep the ponds from freezing. However, the water quality is quite low for other uses (Barroll and Reiter, 1995).

Truth Or Consequences Geothermal Area

The Truth or Consequences geothermal system is the fourth study area in this investigation (Fig. 2.9). One sub-area is the downtown area of the city of Truth or Consequences, formerly known as "Hot Springs," where there are several hot springs. Twelve samples in the city limits are taken from artesian springs and bathhouses that use shallow pumps. A sample is also collected from Los Animas Spring (No. 37), a privately held warm spring northeast of Hillsboro, west of the Rio Grande rift. Four additional samples are collected from another private ranch located on the eastern side of the river (Nos. 38, 39, 40, 41). This ranch is located several tens of miles north-east of Truth or Consequences. A north-northeast trending left-lateral normal fault, the Hot Springs Fault, extends across the property. Sample sites include Deep Well (No. 38), a nonpotable outside water well, Hackberry watering hole (No. 41), which is a cattle-tank supply;

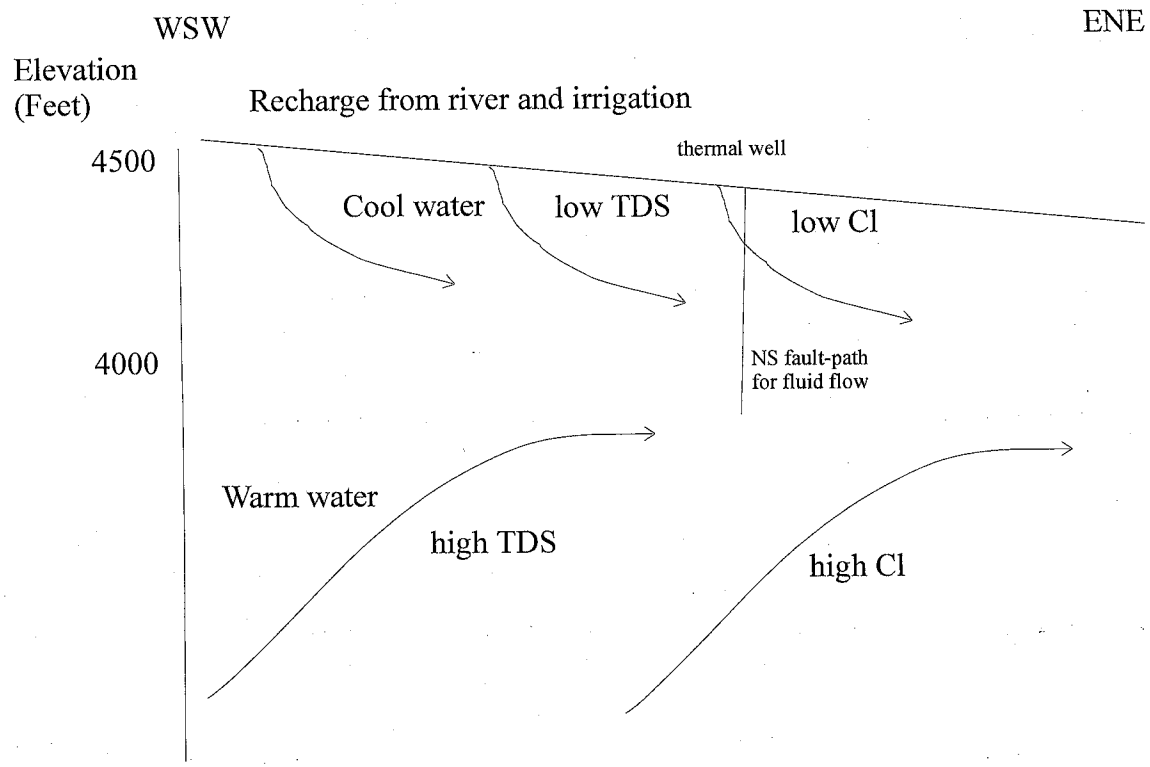


Figure 2.8. Bosque del Apache Cross-section after Barroll and Reiter, 1995.

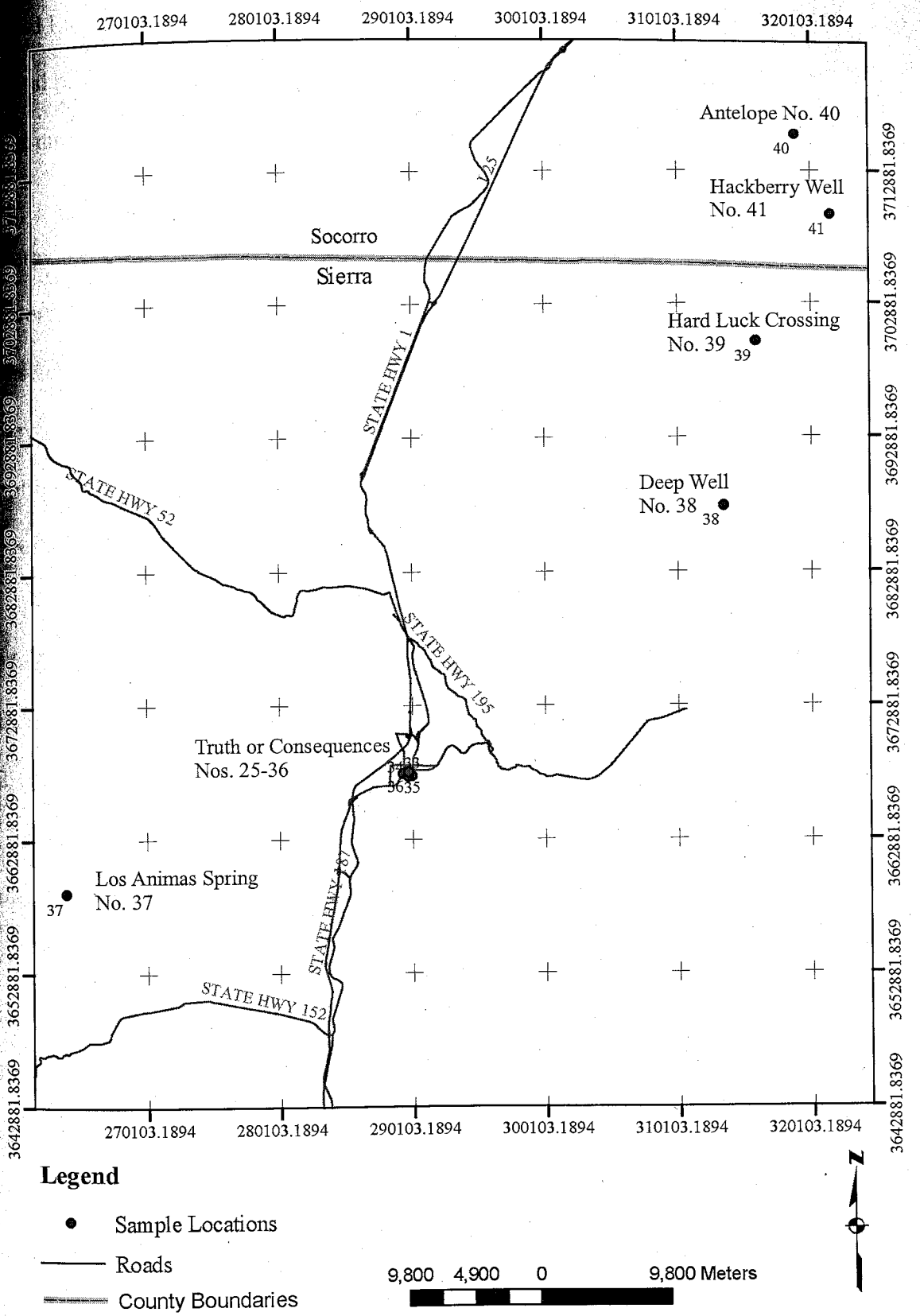


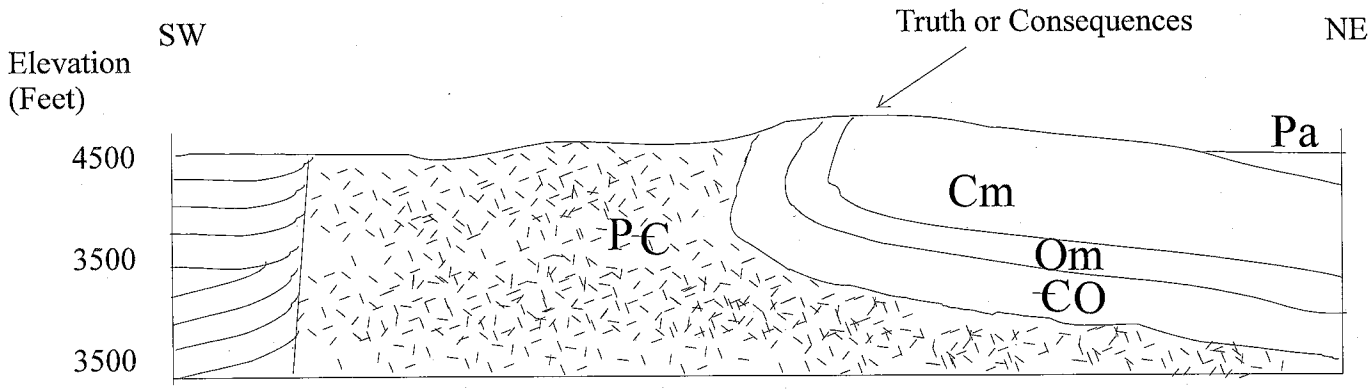
Figure 2.9 Map of the Truth or Consequences Area Showing Sample Locations.

Hard Luck Crossing (No. 39), and Antelope hole (No. 40), the last two are corroded metal pipes from wells that were last used in the early 1900's and have been uncapped and unused ever since.

The Rio Grande is dammed to the north of Truth or Consequences by Elephant Butte Dam. The river formerly flowed through what is now the downtown area, but was diverted as early as the 1880's for irrigation. Precambrian granites and gneisses form the basement rocks. The Cambrian El Paso Group, Ordovician Montoya Group and Devonian Percha Formation are exposed locally in an overturned syncline that has been uplifted and eroded. Syncline thickness is approximately 2000 feet combined, which is overlain by quaternary sediments.

Thermal waters are forced upward along the Devonian Percha and Carboniferous Magdalena Group contact. Many bathhouses and private residences have artesian flow thermal waters. A cross-section of the region after Bushnell et al. (1955) is shown in Fig. 2.10.

Owners of the hot springs bath houses are very proud of the mineral content in their water. Total dissolved solids that are four times higher than in Hot Springs, Arkansas, a fact that is advertised by hot spring owners in their brochures. Most hot springs reportedly contain arsenic concentrations of 50µg/l. This value is reported by a Los Alamos high school science class that determined water chemistry using an ICP-MS at Los Alamos National Laboratories for water from Marshall Hot Springs (Marshall Hot Springs, 2000). Samples from the Artesian Bath House also have arsenic concentrations of 50 µg/l. Samples taken May 31, 1987, were analyzed at the Los Alamos National Laboratory (Artesian, 2000). Charles Motel waters contain 50 µg/l arsenic, which is



Pa Abo Formation

Cm Magdalena Group

Om Montoya Group

€O Bliss Formation & El Paso Group

P€ Precambrian granite and gneiss

Figure 2.10. Truth or Consequences Region Cross-section after Bushnell, 1955.

reported in a mineral content analysis sheet from Los Alamos National Laboratory on samples taken May 31, 1987 (Charles Motel, 2000). Waters at Indian Springs Hot Mineral Bath were analyzed by the U.S. Geological Survey; arsenic content is not reported (Indian Springs, 2000).

METHODS

Arsenic Speciation Kit Development

Columns and Column Configuration

Econo-columns (Fig. 3.1) are obtained for ASK2 kits from BioRad. The columns are made of white translucent polypropylene and have a porous polymer frit at their bases. The lower part of the column is cylindrical, has an internal diameter of 1.5 cm, and is 12-cm tall with a reservoir capacity of 20 ml. The total column length is 14 cm, not including the luer end fitting below the frit. The top of the column has a 2-cm-tall, cone-shaped reservoir that holds 10 ml. Total volume capacity for this column is 30 ml. Stopcocks are fitted to the fitting at the bottom of the column. Glass columns (BioRad) with internal diameters of 1 cm and heights of 10 and 30 cm are used to make ASK4 columns of two different heights (Fig. 3.1). Capacities of short and tall columns are 8 and 24 ml, respectively. Columns are linked in series with the shorter column at the bottom connected by a BioRad female-female luer fitting. The lower column is fitted with a stopcock and the top column is fitted with a 250 ml reservoir funnel.

Seven different column configurations are used in the development of the Arsenic Speciation Kit for two species (ASK2) and Arsenic Speciation Kit for four species (ASK4) methods. For the ASK4 method, 10-cm-tall and 30-cm-tall column are most often used in series, with the taller column on top of the shorter column. The columns are

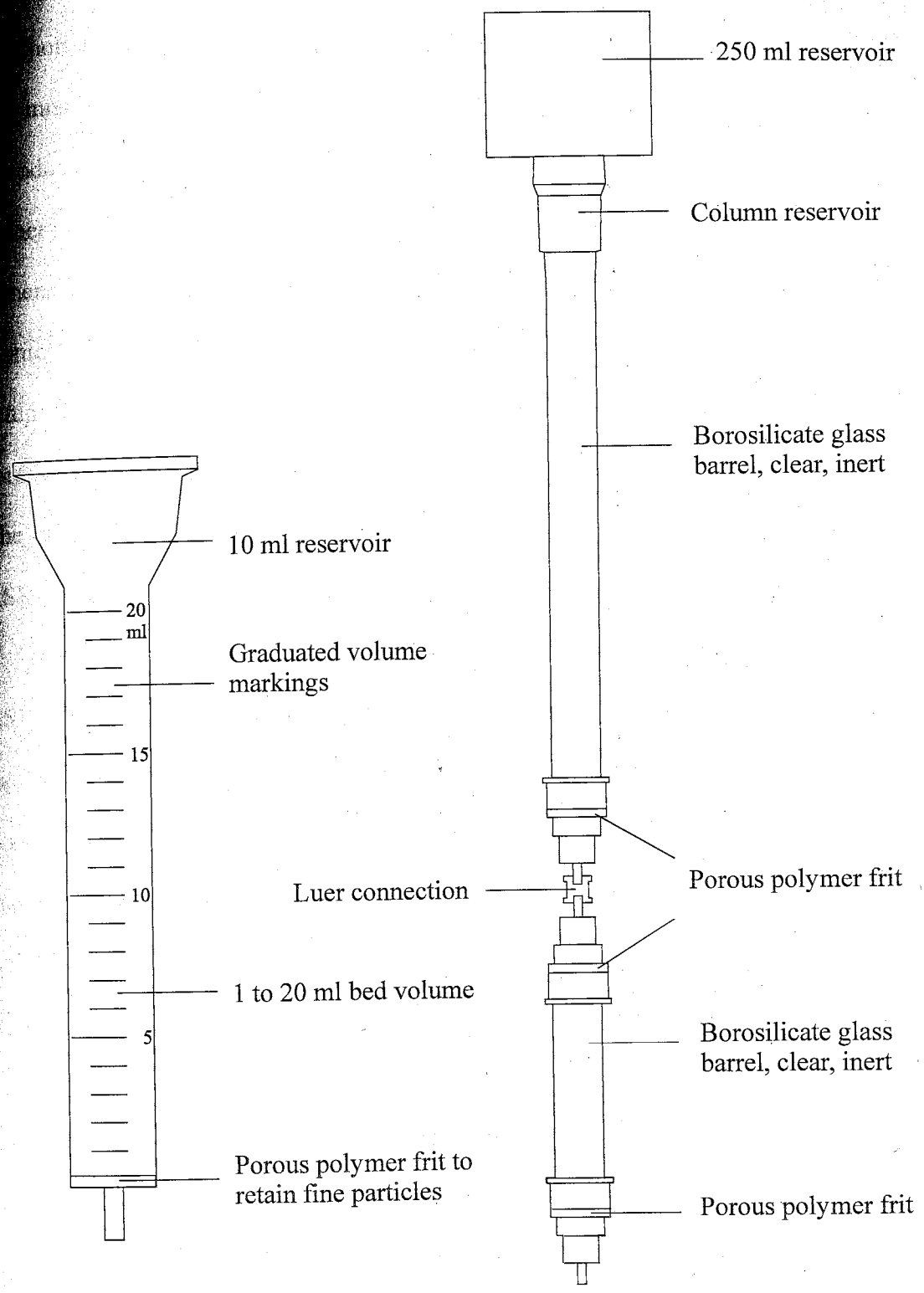


Figure 3.1. Sketch of econo-column (ASK2) and glass columns (ASK4).

also split and used separately, yielding two configurations: one configuration with only the shorter, anion column, and one configuration with the taller, cation column. These columns are mounted on clamps and are fit with BioRad reservoirs for sample introduction. Two other column dimensions are experimented with: a 50 ml buret (e.g. Fisher brand Student Burets with 50 ± 0.10 ml measured markings, approximate dimensions 1 cm internal diameter and 70 cm height) and a column with a 2.5 cm internal diameter and 30 cm tall that we nicknamed the "fat column." Analyses using column setups that deviate from the two-column series setup are distinctly labeled in the data spreadsheets in the appendix. For the ASK2 method, two column configurations are used. The first experiments (~5 in number) use the 10 cm glass column with reservoir that the ASK4 method uses. Most experiments are done using the econo-column.

Clampstands and clamps to hold the columns are set up on a laboratory bench. ASK4 columns are labeled numerically and sequentially with a permanent marker to keep track of which experiments are performed on the individual resins in the columns. A log is kept in the common logbook for all columns; this includes details on the experiments that are done for each column and when the resin is regenerated. Cation resin for the ASK4 method is slurried into the tall (cation) column to a height of 25 cm. The short column is filled with anion resin, capped, and hooked in series to the cation column via a luer fitting. Resin for the econo-column ASK2 experiments is slurried to the 15-ml volumetric mark on the column. A frit is fitted snugly to the top of the resin to keep resin from spilling during transport or becoming disturbed during sample introduction. A stopcock is fitted to the tip of the column on the bottom.

Exchange Resins

For the ASK2 experiments, analytical grade chloride-form strong anion exchange resin with 100-200 mesh size (AG1-X8 strong anion exchange resin) is obtained from BioRad. The resin is made up of a styrene ($C_2H_3C_6H_6$) divinylbenzene ($(C_2H_3)_2C_6H_6$) copolymer lattice (BioRad 1999). The resin has a crosslinking of 8X, which means that the resin resists changes in volume with changes in hydration and has a lower bead pore size than other resins available through BioRad (BioRad 1999). The AG1-X8 resin that is used in these experiments is recommended for exchange, sorption, and separation of inorganic anions with low (< 800 g/mole) molecular weights (BioRad 1999). Medium mesh (100-200) is recommended for either column or batch separations (BioRad 1999). Chloride resin is batch-converted to acetate form by soaking the resin in a 1 M NaOH (trace metal grade, Fisher Scientific) solution for 30 minutes. The resin is decanted and rinsed with RO water, then is soaked for 30 minutes in a 1 M acetic acid solution. This procedure is repeated three times. After the final decanting of acetic acid, the resin is rinsed with RO water three times. Effluent RO water from the final rinse is checked for resin conversion by adding a few drops of 1% $AgNO_{3(aq)}$ to a small sample (< 5 ml). An incomplete conversion would contain Cl^-, which complexes with Ag^+ to form $AgCl_{(s)}$. Converted resin is saturated in RO water and stored in covered beakers that are labeled with the date of conversion and the lab technician' initials.

For the ASK4 experiments, BioRad AG1-X8 50-100 mesh strong anion exchange resin in chloride form and AG1-X8 50-100 mesh strong cation exchange resin in hydrogen form are obtained. Resins are used in the received ionic form. Resins are stored in the original containers until portions of resin are slurried in RO water and stored in

covered beakers. Resins are regenerated before initial use and after each experiment. Regeneration included passing a series of eluents through the column and finally equilibrating the column to the pH and eluent that will be introduced into the column. The order of eluents used follows: 70 ml 1.5 M NH_4OH, 70 ml 1.0 M HCl, 70 ml 0.48 M HCl, 70 ml 1.5 M NH_4OH, 70 ml 1.0 M HCl, 70 ml 0.48 M HCl, and 40 ml 0.2 M TCA. Regenerated resin is stored in columns with a small volume of 0.2 M TCA on top of the resin to keep the resin saturated.

Arsenic Standards

Solid arsenic standards are obtained as sodium arsenate, $Na_2HAsO_4 \cdot 7H_2O$ (As(V), Sigma-Aldrich); arsenic trioxide, As_2O_3 (As(III), Sigma-Aldrich); disodium methylarsonate (MMA), $CH_3AsNa_2O_3 \cdot 6H_2O$ (donated by Dr. Dean Carter, Arizona State University); and sodium cacodylate (DMA), $(CH_3)_2AsO_2Na$ (Sigma-Aldrich). Chemical purities are reported at 99.99%, 100.0%, unknown, and approximately 98%, respectively. Solid samples are stored in a desiccator. The As(V) standard is prepared by weighing 4.1646 ± 0.0001 g sodium arsenate (QA Mettler AE 163 balance using Fisher Scientific weighing paper) and dissolving it in a 1.00 ± 0.001 l volumetric flask with a mixture of less than 10 ml of 12 M trace metal grade HCl (Fisher Scientific) and reverse osmosis water (RO; double-distilled water is filtered through a reverse osmosis Milli-Q millipore pack). All glassware is Class A volumetric glassware. The 1 g/l As(V) standard is used to make 100-µg/l and 50-µg/l standards by pipetting 50.00 ± 0.05 ml into a 500.00 ± 0.20 ml volumetric flask and 25.00 ± 0.03 ml into a 500.00 ± 0.20 ml volumetric flask and diluting with RO water. Stock concentrations of 20 µg/l, 10 µg/l, 5 µg/l, and 2 µg/l are

pared in similar fashion. All volumetric flasks are sealed with parafilm. A 1 g/l methylarsinic acid arsenic standard (MW 160.0 g/mole) is prepared by weighing 8566 ± 0.0001 g and dissolving it in a 1 liter volumetric flask with HCl-acidified RO water as described. Subsequent DMA dilutions are made from this stock solution. An MMA solution is made using 0.2027 ± 0.001 g sodium methylarsonate (MW 292.0258 g/mole), yielding a 52 µg/l MMA standard. Arsenite is prepared as needed; a 1 g/l stock solution is prepared using 1.3203 ± 0.0001 g arsenic trioxide (MW 197.84) per liter of HCl acidified RO water. Hydrogen peroxide (30% in water, reagent grade) is used to reflux some of the As(V) standard to ensure it contained no organic arsenic.

Analytical Reagents

The separation for the ASK2 requires hydrochloric, sulfuric, and acetic acids. The column eluent is a 0.12 M (10%) hydrochloric acid solution, trace metal grade 12 M HCl (Fisher Scientific, w/w 35.0-38.0%) that is obtained and diluted volumetrically. Eluent is generally made up in 1 liter volumetric flasks and stored in 1 liter, acid washed, trace clean, Nalgene bottles. A 10% sulfuric acid solution is prepared using trace metal grade (Fisher Scientific) H_2SO_4 for acidifying field samples. Trace metal grade acetic acid, CH_3COOH, (Fisher Scientific, 99.5% w/w) is obtained for resin conversion.

For the Arsenic Speciation Kit for four species (ASK4), the following reagents are used: trichloroacetic acid, hydrochloric acid, and ammonium hydroxide. A 0.006 M trichloroacetic acid (TCA; analytical grade) is prepared by dissolving 9.803 g TCA in 10.00 l RO water. The water is measured in 1.00 ± 0.006 l graduated cylinders. Total error is 10.00 ± 0.060 l. Solutions of NH_4OH (trace metal grade, Fisher Scientific) are

prepared in 1.5 and 3.0 M concentrations using 1013 and 2026 ml per 10.00 ± 0.060 l, respectively. Volumes are pipetted using the largest graduated cylinders and pipettes possible (e.g. a 1.00 ± 0.006 l graduated cylinder, a 10.00 ± 0.02 ml, and 3.00 ± 0.01 ml pipette for a cumulative volume of 1013 ml and error of ± 6.03 ml). Reagents are stored in 15 liter carboys that are cleaned using a 24-hour soak in a 10% nitric acid solution and triple rinsed with RO water.

Column Separation Method: ASK2

Econo-columns are slurried with resin as described above and mounted on clamps attached to the workbench. An OHAUS Analytical balance with capacity 200 ± 0.01 g is placed beneath the column. The column height is adjusted on the clamp so that a sample cup could sit on the scale and have approximately 2 cm clearance below the stopcock on the column. Where possible, aliquots are captured directly in the 2 ml polystyrene sample vials (CPI International) that are used in the GFAA autosampling carousel. If larger aliquots are sampled (e.g. samples larger than ~2.2 ml), samples are captured in larger, acid washed vials and a part of the sample is analyzed.

Any fluid sitting on the top of the frit is drained through the column and discarded. Samples are introduced into the top of the column from a pipette or graduated cylinder. Samples are generally introduced in a large slug and refilled as the column drained if the entire sample would not fit in the top of the column reservoir. The sample is drained out of the column in small increments (generally 2 to 10 ml), captured for analysis, and weighed in tared sample cups. Sample masses are recorded in the joint log book after each aliquot is captured. After all of the sample volume passed through the

olumn, a small volume (~ 2 ml) of eluent is added to the top of the column. The eluent or ASK2 separations is a 0.12 M HCl solution that has been described. The small volume is to flush any remaining sample through the resin rather than dilute any arsenic that may be present with a large aliquot of eluent. After the eluent passes through the column and the meniscus hits the top of the frit, a larger volume of eluent is introduced into the column, generally as much as the column will hold on top of the resin (~ 20 ml). Eluent samples are collected continually in the same manner as the arsenic sample aliquots. The flow rate varied slightly from column to column. The resin compresses as HCl is added, so the flow rate slows as the experiment progresses. When small aliquots (~2 ml) are taken, the length of time required to perform a speciation analysis (25 ml sample and 75 ml eluent) in a run is on the order of 45 minutes. It takes approximately 20 minutes to perform column separation and capture two aliquots. The effects of capturing 50 aliquots vs. two aliquots are specifically investigated and have no noticeable effect on the results. Flow rate adjustments are not made, flow is gravity driven and stopped only for the transition from sample to eluent and for changing sample collection bottles. The effects of changing flow rate on the elution point of arsenic is not specifically investigated. Flow rate fluctuations appear to be negligible but are noted as present within a single column due to pH-dependent resin compaction, and from column to column due to differential packing.

Recoveries are calculated for all column experiments. The mass of each sample is multiplied by the concentration in the aliquot of sample, resulting in a mass of arsenic for each sample. The masses are summed and compared to the known mass of arsenic introduced to the top of the column. For field samples, where arsenic species and

concentrations are unknown, the ASK2#1 and ASK2#2 aliquots are compared to the filtered, acidified sample that is taken to analyze total arsenic and other metals. Each ASK2 sample has twice the volume (50 ml each) of the aliquot introduced into the column (25 ml), samples are normalized to the introduced sample aliquot by doubling the concentration that is reported for each ASK2 sample. GFAA data is shown in appendix A.1

All samples are grouped in "runs" representing an elution from a single column. These runs are labeled using the month, year, and an alpha numeric. This resulted in the following type of label: MMDDYYA. A run could contain as few as two samples or as many as 80, depending on the goal of the analysis.

Arsenic Field Speciation: ASK2 Method

Water is collected and arsenic species are separated following the ASK2 method described above. The following modifications are made for field work: The ASK2 column is mounted in a portable ringstand and placed on a rollout table or other clean flat surface. The ASK2 sample bottles are labeled with the site identification, date, analyst, and ASK2#1 or ASK2#2, depending on which aliquot is being captured. A 25 ml water sample is drawn into a 50 ml syringe (e.g. Fisher), filtered through a 0.45-µm in-line syringe filter (e.g. Corning 25 mm diameter, 0.45-µm and hold-up volume of <60 µl, individually packed filters), and expressed into a 30 ml acid washed plastic collection cup. The sample is then acidified to ~ pH 2 (checked using pH paper) using a 10% sulfuric acid solution. Approximately three drops are required. The acidified sample is then introduced to the top of the column and eluted, followed by a 25.0 ml aliquot

measured in a 25 ml graduated cylinder) of 0.12 M hydrochloric acid, and collected in a 50 ml ASK2#1 sample bottle. A 50.0 ml aliquot of 0.12 M hydrochloric acid (measured in a 50 ml graduated cylinder) is passed through the column and captured in the ASK2#2 50 ml sample bottle.

Column Separation Method: ASK4

The analytical separation method for investigating the speciation of arsenic using the 4-species method is very similar to the ASK2 method. Resins are slurried into the columns as described and mounted to the clamps on the workbench; the OHAUS scale is used to measure sample masses as they eluted from the column. Any fluid above the resin height is drained through the resin and discarded. Generally, samples are introduced into the top of the column using a pipette and eluent volumes are measured using graduated cylinders. The reservoir on the ASK4 columns is much larger than the largest eluent volume, and eluents are generally introduced in large slugs with the exception of the first eluent to follow the sample and the first few milliliters of each new eluent being introduced. For example, a 5 ml arsenic standard would be introduced into the top of the column from a pipette. Samples would be collected as fluid passes through the column. The first eluent, 0.2 M TCA, would be introduced in two steps. The first sample introduction would consist of only a few milliliters (<5 ml), and introduction is generally done by pouring from the graduated cylinder along a glass rod that would be placed into the sample reservoir. This slowed the flow of fluid and minimized disturbance of the resin. After the meniscus of eluent reached the top of the resin, the remaining eluent would be added slowly using the glass rod as a pouring guide. After this eluent volume

passed through the column and the meniscus touched the top of the resin, the next resin would be added in similar manner. The approximate time for all eluent to pass through the column is generally in excess of one hour. Flow rate is gravity driven and dependent on resin compaction, fluid column height, and resin pH. Anion resin tends to shrink in low pH, lowering the flow rate.

Arsenic Analysis Method

For the determination of arsenic, samples are analyzed using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAA) at the New Mexico Bureau of Mines, following EPA Method SW-846 7060A. Quality Assurance and Quality Control (QA/QC) parameters for this method are contained in Method 7000A (EPA, 2001e,f). The method allows for deviation of the strict quality control and assurance guidelines as long as calibration, linearity, and other parameters are documented, but prohibits reference to the method without further explanation. Samples are analyzed using SW-846 7060A, with modification in some cases.

Total arsenic is determined in aqueous samples using a SpectrAA-600 GFAA with autosampler. The calibration standard and samples are analyzed in triplicate. Sample platform is Varian 10x Partition tubes. A single element arsenic hollow cathode tube lamp with wavelength 193.7 nm is used. Zeeman background correction is used for all arsenic analyses. Zeeman background correction is a method of auto-correcting background interferences that are common with elements that have low analytical wavelengths, and is strongly recommended for GFAA arsenic analyses (EPA, 2001e). Samples are auto-injected into the graphite tube with an equal volume of nickel nitrate

modifier (200 ppm $NiNO_3$), dried, and ashed. The GFAA software determined the calibration graph (> 0.998 correlation required) from autodiluted stock standard. The calibration is resloped every 12 samples and recalibrated every 25 samples. An external arsenic standard consisting of a 1/10 dilution of EPA standard 1643d, with known arsenic concentration of 5.6 µg/l, is analyzed in many of the runs. Makeup water blanks, arsenic standards that are made up for column experiments, reagents, and furnace calibration standards are analyzed in many runs as external calibration checks. External calibration checks are not analyzed in every batch of samples.

The method we employed for analyzing arsenic differs only slightly from EPA method SW-846 7060A in that we did not employ duplicate analyses (same sample twice in one run) and external standards for all analyses. All other criteria, including reslope and restandardization frequency, are met. The EPA method requires 2 replicates per sample, we analyzed in triplicate.

The GFAA is capable of detecting total arsenic and makes no distinction between species. Error is automatically calculated by the GFAA, and a root mean squared error is reported for each analysis.

Error Assessment in Arsenic Analyses

Analytical Measurement Error

Analytical measurement error is the cumulative error associated with making basic measurement using balances and volumetric flasks. A propagated error calculation for the preparation of the As(V) standard is as shown: A 4.1646 ± 0.0001 g sodium

arsenate is dissolved in a 1.00 ± 0.001 l volumetric flask. If the balance weighed a low mass (4.1645) and the volumetric volume is high (1.001 l), then the concentration of arsenic in the 1 g/l As(V) standard is:

(312.013626 g/mole sodium arsenate)/(4.1645 g) = 74.9222 g As

74.9222 g As/1.001 l = 0.9990 g/l As

resulting in a 0.1% error. If this standard is diluted using a 50.00 ± 0.05 ml pipette and a 500.00 ± 0.20 ml volumetric flask, then assuming low mass and high dilution error:

(49.95 ml) * (0.9990 g As/l) = 500.20 ml * concentration

concentration = 0.09976 g As/l

resulting in a ± 0.24% estimated cumulative error to this point.

Additional error can be assumed any time glassware is not used at the calibrated temperature of 20°C, which is the guaranteed accurate temperature of TD and TC volumetric glassware. If the temperatures are greater than 20°C in the laboratory, then liquids will have lower densities and dilution concentrations will be systematically lower than calculated. Error can also arise in the transfer of sample from weighing paper to the volumetric flask due to retention of dry sample on the weighing paper. Another systematic measurement error is associated with calculating volumes by weighing samples and assuming a density of 1.00 g/ml. The density of 0.12 M HCl is 1.00365 g/ml. Assuming the eluent does not participate in ion exchange processes, the introduced error results in 0.365% volume underestimation and is considered a minor systematic error.

Reagent Purity Error

Error from reagents has two potential sources. First is the purity of the reagent. Purities are listed by the manufacturer for all reagents with the exception of MMA. Another potential source of error is the hydration of standards. If standards are not desiccated and water is incorporated into the solid samples, then the masses weighed on the analytical balance will contain less arsenic and more water than calculated. This is expected to be a minor error in these experiments because the humidity in Socorro is extremely low and samples are stored in a desiccator.

Theoretical GFAA Error

Instrument error is difficult to pinpoint and has many potential sources. It is recognized by the EPA that arsenic is one of the most difficult elements to quantitatively analyze in water. Therefore, the quality control parameters for validating arsenic concentrations in water samples are outlined precisely. A calibration reference standard must be within 20% of known true value for the calibration curve to be valid (EPA, 2001f). One of the simplest types of analytical error is due to absorption interferences by other elements that may be present in the sample. Acidified RO water samples are used in the development of the ASK2 method and no ion interferences are expected. Samples that contain concentrations of arsenic near the detection limit of the GFAA (~ 2 μg/l) are subject to type one analytical error: reporting of false positives in blanks. This type of error is likely to be significant in our analyses. Arsenic is calibrated using the autodilution function of the GFAA sampler. Dilutions are made by inserting a plastic tube (< 1mm diameter) into the standard cup holder, the tube is coiled inside of the

autosampler, the tube is connected to a reservoir of acidified RO water and a microsyringe. The syringe moves in a glass column, and the distance that the syringe moves inside the glass column is proportional to the volume the sample tube picks up. Air bubbles are expelled from the sample tube prior to beginning every arsenic analyses to ensure accurate volume measurements. Error from this source is expected to be minor. Further error can be introduced in the form of instrumental drift. All analytical machines are subject to some drift in calibration and should be re-zeroed and resloped if not recalibrated periodically. Sample batches are resloped after every 12 samples and recalibrated after 25 samples. Therefore, error is expected to be minor from these sources. Another source of error is the standard and standardization method. Standards are prepared in the form of As(V) from an aqueous atomic absorption standard. Calibration standards are acidified with trace pure nitric acid and diluted using RO water. The GFAA detects total arsenic present using hollow cathode arsenic lamp emissions to detect (in the monochrometer) interference as the sample is ashed. It is unclear what the effect of using an As(V) standard is on analyzing for another arsenic species. Several researchers have observed that MMA standards gave lower concentration readings than expected when they used an As(V) calibration standard (Meng in press; Grabinski 1981). Systematic species detection error is investigated in the Results section of this paper. Another source of error is from the standard matrix: samples are passed through an anion exchange resin (ASK2) or anion and cation exchange resins (ASK4) before being analyzed. Therefore, samples are no longer in RO water, but are in a mixture of hydrochloric acid and water that has been passed through the resin. It is unclear what the effect of this difference in matrix (RO water standard vs. hydrochloric acid-exchanged arsenic spike sample) has on

arsenic detection. Standard dilutions for the calibration graph are made using make-up water. Make-up water is water that contains no arsenic but has the chemical make-up of the sample water. Three types of make-up water are employed during arsenic analyses on this project: RO water, eluent, and matrix water. The eluent make-up water consists of using an aliquot of the eluent that is being passed through the column as make-up water. In most ASK2 analyses, 0.12 M HCl is used as make-up water. Matrix water is used occasionally for analyses from the ASK4 method. A blank sample is introduced into the column, and eluents are passed through the column during regular separation. Eluent is collected in aliquots that represent the volumes where the arsenic standards would elute. This eluent is labeled according to species (e.g. As(III) make-up water) and used as make-up water.

Actual GFAA Error

One hundred forty external reference standards are analyzed in ASK2 and ASK4 runs. Error is calculated by comparing the known standard value to the value the GFAA reported. Of the 140 external reference standards, 57 (constituting 40%) deviated less than 5% from the known value. One hundred thirty (93%) had errors that are less than 36%. The average absolute value of the error is ±11.4%. Only 7 % of external reference standards had errors larger than 36%. The error in these cases is related to runs of external standards that are performed in order to verify whether or not the standards are good. In all cases, unexpectedly high or low run results had caused us to check the standards and dispose of them as necessary. These data are summarized as Appendix C.

Recovery Calculation Error

The theoretical maximum acceptable GFAA error is compounded when recoveries are calculated. When the concentrations of ASK2#1 and ASK2#2 aliquots are doubled to normalize to the standard volume, the error is increased by ±13.4% over the ±20% MS/MSD the EPA requires for GFAA As analyses, resulting in a total potential analytical error of ±33.4%. The derivation of this result is shown in this sample calculation: if both the ASK2#1 and ASK2#2 sample had actual concentrations of 10 µg/l, the reported GFAA values could range from 8 to 12 µg/l and be acceptable. If the total arsenic sample (from the filtered, acidified replicate) had a concentration of 40 µg/l and reported on the highest acceptable value (48µg/l), and both ASK2 aliquots reported low values (8 µg/l for both), then:

[(Normalized ASK2#1 + Normalized ASK2#2)] / total replicate *100% =

= [(2 * 8 µg/l) + (2 * 8 µg/l)] / 48 µg/l * 100% = 66.6%

Contamination Error

Contamination is the final form of error to be considered. The greatest source of contamination in the laboratory is from tap water. The tap water in the lab is analyzed numerous times. The arsenic concentration ranges from 20 to 40 µg/l. Hot tap water yields consistently lower arsenic concentrations than cold tap water. Glass- and plasticware are rigorously cleaned after each use by soaking in a 10% nitric acid bath (trace metal grade nitric acid) and triple rinsing with RO water. Glassware is either air-dried on paper towels or dried in an oven. Pipettes and graduated cylinders are stored in sealed Ziploc bags when not in use. Paper towels used to dry glassware on are analyzed

for arsenic. A few sheets are boiled in acidified (nitric acid) RO water, the analysis shows that no arsenic is present in the paper towels. Because tap-water arsenic concentrations are around 40 μg/l, it is not expected that contamination is a major source of error because rigorous laboratory practices are followed.

Summary of Overall Error

Errors in the quantification of total arsenic and arsenic species are expected to be greatest from instrument error, which can exceed ± 20% for arsenic analyses or 33% when ASK2 samples are compared to total arsenic samples. While it is impossible to assign a maximum error value, cumulative error in the determination of arsenic in samples likely approaches an outer limit of ± 35%. Overall, errors in the analytical method are expected to be the greatest of all forms of error possible.

Field Sampling

Sampling was carried out between January and September, 2000. Sample locations are shown in Fig. 2.2. Water is sampled by hand into acid-washed Nalgene bottles. Four separate samples are collected at each site: one for trace metal analysis, one for nonmetal analysis, and two samples (ASK2#1 and ASK2#2) for arsenic species analysis. Trace metal samples are filtered through a 0.45μm filter and acidified to pH <2 with ultra-pure nitric acid within 24 hours of collection. Nonmetal samples are not treated at the time of collection. A portion of untreated sample is filtered through 0.22μm filter paper for analysis by the Ion Chromatograph (IC).

Field Sampling Equipment and Procedures

Meters for pH, Eh, conductivity, and temperature are used in the field. The pH is measured using an OAKTRON pHTestr2™ meter. A 2-point calibration and calibration check is performed prior to testing each sample using pH buffers 7.0 and 10.0. The range is -1.0 to + 15 with resolution of 0.1 pH and relative accuracy ± 0.1 pH (Oaktron, 2001a). The operating temperature range for the pHTestr2™ is 0°C to 50°C (Oaktron, 2001a). The Eh of samples is measured using an OAKTON ORPTestr™ meter. The Eh meter is a noncalibrating meter with a range of -50 mV to +1050 mV, with a resolution of 5 mV and accuracy of ± 150 mV (Oaktron, 2001b,c,d). The ORPTestr™ reads absolute mV and needs no conversion or compensation, e.g. due to the reference Ag/AgCl electrode, to give Eh units. The operating temperature range for the ORPTestr™ is 0°C to 50°C. Conductivity is measured using an OAKTON TDSTestr 1™ meter. The conductivity meter is temperature compensating with an operating temperature range of 0°C to 50°C, has a range of 0 to 1990 ppm with a 10 ppm resolution and 2% full scale accuracy (Oaktron, 2001e). Temperature is measured using a digital temperature gauge that has a three digit readout (e.g. 55.2°C) and an accuracy of ± 0.1°C.

Alkalinity is measured in the field using a LaMotte brand alkalinity test kit with a direct read microburet in 4 ppm HCO_3^- increments. An untreated sample is introduced into a calibrated cylinder. A tablet of Bromocresol green is added to the sample. The sample is capped and swirled until the tablet dissolved. Sulfuric acid from the test-kit is added using a 1.0 ml microburet until a color change from blue to pink is observed while swirling the sample. The ppm bicarbonate concentration is read directly off the calibrated syringe. Minimum error is approximately ± 4 ppm.

A Garmin 12XL Global Positioning System (GPS) unit is used to determine Universal Transverse Mercator (UTM) coordinates for most sample sites. Accuracy for sampling locations is ± 15 meters. UTM coordinates are omitted where the receiver did not locate sufficient number of satellites to determine the position. All sample sites are located in UTM Zone 13, the Datum is NAD27 CONUS (North American Datum, year 1927, Continental United States).

Laboratory Analysis of Field Samples

Laboratory analyses are performed at the Bureau of Mines and Mineral Resources Wet Chemistry Lab. Arsenic samples are measured from the metals samples (filtered and acidified field duplicates) and analyzed using the GFAA as described earlier. Cations are analyzed on an Instrumentation Laboratory brand AA/AE (Atomic Absorption/Atomic Emission) Spectrophotometer (FAA) using direct aspiration measured in absorbance. Established EPA methods are followed for all elements analyzed and are listed with their detection limits: Silica, Method 3111D (10 ppm); calcium, Method 215.1 (0.2 ppm); sodium, Method 273.1 (0.1 ppm); potassium, Method 258.1 (0.2 ppm); lead, Method 239.1 (0.1 ppm); iron, Method 236.2 (0.2 ppm); manganese, Method 243.1 (0.1 ppm); and magnesium, Method 242.1 (0.1 ppm) (EPA 2001g). Silica, lead, and iron are analyzed using filtered, acidified samples and triple-expanded calibration scales to enhance low level detection; all other ions are analyzed using unfiltered samples and a standard FAA calibration scale. Sodium and calcium are reanalyzed on a Varian SpectrAA 110 Atomic Absorption Spectrometer equipped with a 60 slot autosampler and autodilution. Both FAA instruments use single element hollow cathode lamps. All

standards are prepared from 1000 mg/l stock single element solutions. Standards are chosen so all values would fall within the calibration range. Where sample concentrations are out of an acceptable calibration range, samples are diluted volumetrically using analytical grade pipettes and volumetric flasks. Sample concentrations are calculated by the FAA using the average of 5 readings per sample; error is autocalculated and is less than 5% on all reported values. For samples analyzed on the manual SpectrAA, external calibration checks are frequently performed (at least every 5 samples) using calibration standards. Calibration is auto-zeroed and auto-sloped using a midrange calibration standard at least once every five samples. Usually, more than five samples are analyzed in duplicate every set of 47 samples.

Anions are analyzed using a Dionex AS50 Ion Chromatograph with Autosampler, CD25 Conductivity Detector, and GS50 Gradient Pump. Conductivity detection is used to analyze the concentrations of the following ions: fluoride, chloride, nitrate, sulfate, bromide, and iodide. A mixed ion chromatograph reference standard consisting of 91.5 ppm SO_4, 40.5 ppm Cl, 1.52 ppm NO_3, 0.75 ppm F, and 0.6 ppm Br is used as an analytical standard and external calibration check. The standard is autodiluted for calibration. Duplicates and calibration checks are performed in compliance with EPA method 300.0 (EPA 2001g).

RESULTS

The first part of this section describes the evolution of the ASK2 and ASK4 methods. Forty-nine sets of samples are analyzed in the development of the ASK2 method, all of these files are shown in Appendix A. One-hundred-sixty sets of samples are analyzed in the development of the ASK4 method, all of the files are shown in Appendix B. In the appendices, all spreadsheets contain calibration data from the GFAA, arsenic concentrations, and corresponding eluent masses. Graphs are plotted showing arsenic concentration vs. eluent mass. Recoveries are calculated and shown in all spreadsheets.

Development of the ASK2 Kit

The first step in the development of the ASK2 kit is to test previously published methods. We chose to use the method described by Ficklin (1983) as our starting point. This method is described in the previous chapter. Forty-nine batches of analyses are performed. Analyses representative of the evolution of our modifications to the method are chosen here for detailed discussion.

Testing the Adapted Ficklin Method

Chloride-form 100-200 mesh resin (BioRad) is slurried into 10 cm tall by 1 cm diameter glass columns, the top of the column is connected to a 250 ml sample holding cup, a variation on the schematic shown in Fig. 3.1. The volumes required to convert chloride-form resin to acetate-form resin is as follows: 6 ml 1.0M NaOH, 30 ml H_2O, and 10 ml 1.0M CH_3COOH. A 5-ml arsenic species standard is introduced into the top of the column. All eluent is collected in approximately 2-ml aliquots. The volume of the samples is calculated by weighing the eluent in tared sample cups. A single 45-ml aliquot of 0.12 M HCl is introduced into the column after the arsenic sample is eluted. Flow is stopped only for eluent collection. Samples are analyzed for arsenic. The procedure is repeated for each of the four arsenic standards. The results, interpretation, and a discussion of this adaptation are published in Miller et al. (2000) and summarized below.

Results

The As(III) standard elutes in the 2 to 14 ml range with detection of arsenic below the detection limit of 2 µg/l for the 16 to 18 ml range, with an unexpected spike from 20 to 32 ml (Fig. 4.1). Both MMA and DMA elute primarily between 0 and 20 ml (Fig. 4.1), which is the range that should contain exclusively As(III). A portion of the DMA and As(III) standards eluted from 15 to 35 ml (As(III)) and 26 to 34 ml (DMA), which should contain only As(V). Arsenic(V) elutes at approximately 32 ml and ends at 38 ml (Fig. 4.1). Samples are shown in Absorbance and are measured using RO water as matrix. The goal of the analyses is to show the elution points, not quantify the species.

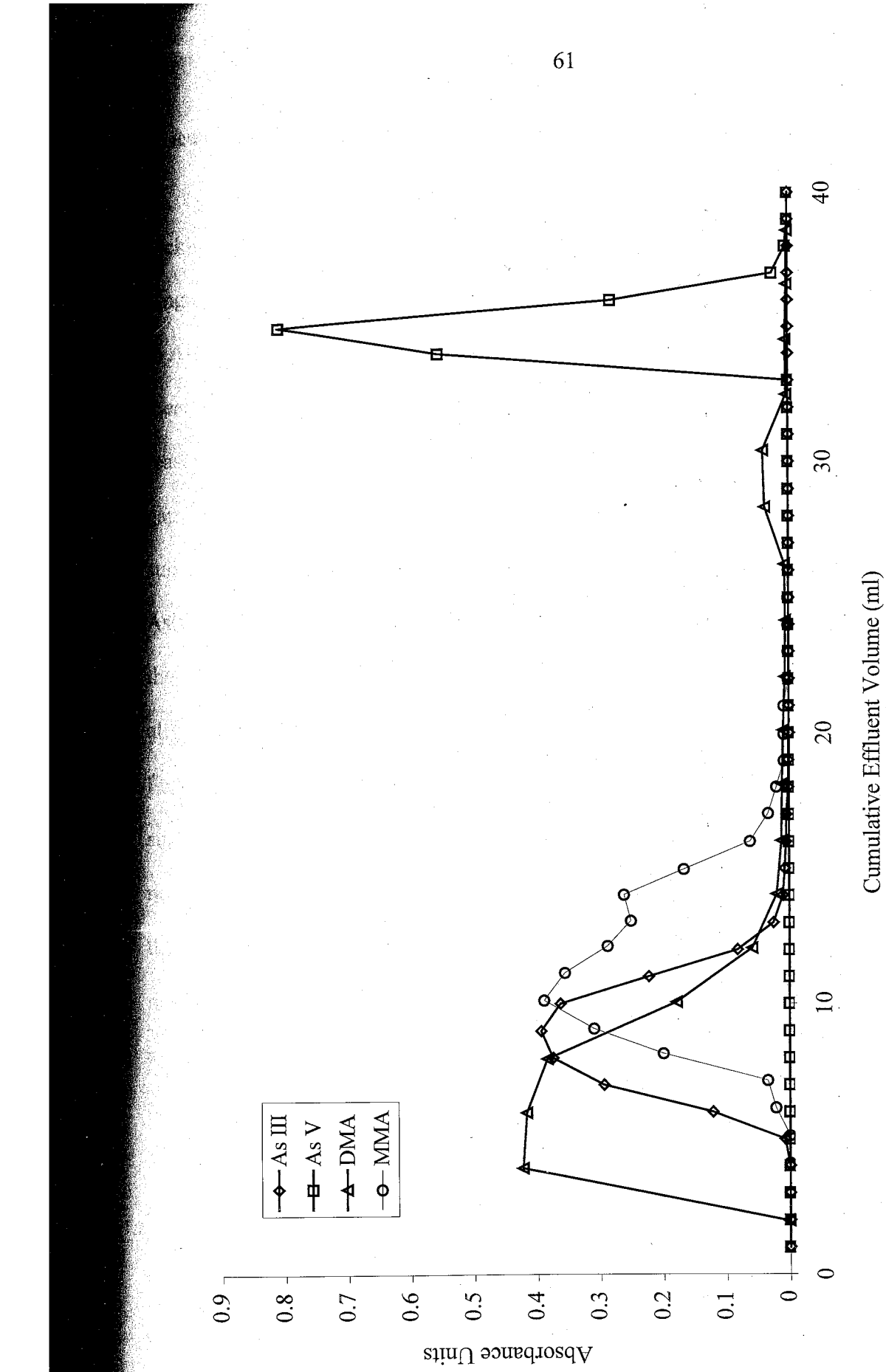


Figure 4.1. Results of the Adapted Ficklin Method, showing As(III), As(V), DMA, and MMA breakthrough curves.

Discussion and Interpretation

The investigation shows several significant flaws with the method reported by Ficklin (1983). First, As(III) elutes in the same range as As(V) in addition to the expected range. One possibility for the As(III) elution in the As(V) range is the oxidation of As(III) to As(V). If As(III) partly or completely oxidized to As(V), then the analysis shows that there is separation of the two species. However, if As(III) conversion to As(V) is the reason behind poor separation, then As(V) elutes at 18 and 28 ml, which is a significant gap. To minimize the potential As(III)/As(V) conversion problem, As(III) standards are subsequently labeled with a date and used as soon as possible. Second, the recovery for As(III) is over twice as high as it should be. One explanation for the high recovery is that the standard could have been prepared using the wrong dry weight of arsenic trioxide. An alternate explanation is that the dilutions could have been miscalculated or mislabeled. Fresh standards are prepared for subsequent analyses and no subsequent analyses show such high recoveries. Third, the organic species MMA and DMA elute in the As(III) range. The interpretation is that DMA and MMA behave similarly enough to As(III) in the acetate resin that no distinction between species can be made. If organic arsenic is present, it will coelute with As(III). If this interpretation is correct, then As(III) cannot be distinguished from MMA or DMA using this method. Any quantification of As(III) must include the warning that any MMA or DMA that may be present is included in this aliquot. Fourth, arsenic is detected at some level in all eluent samples. A clear cutoff volume for As(III) and beginning volume for As(V) cannot be quantified because the species overlap enough in their elution ranges.

Conclusions

The qualitative separation of species using this method is poor. The qualitative separation of As(III) and As(V) is of greatest concern. The first factor that is investigated is the resin. A review of the BioRad resin conversion directions revealed that the resin is likely not converted fully to the acetate-form following Ficklin's method.

Testing a Modification to the Resin I

The next set of tests focused on changing a single variable: resin conversion. These analyses are performed on resin that is converted using the batch method described in Methods under Ion Exchange Resins (p. 41). Resin is slurried into columns like in the previous set of experiments. Standards for separate species runs are introduced into separate columns, the MMA experiment is done twice. A 5-ml aliquot is introduced into the top of a freshly made up column. The sample is eluted and a 35-ml aliquot of 0.12 M HCl eluent is added. All samples are ~2 ml, like the previous experiment. An additional 40-ml aliquot of 0.12 M HCl is added to the As(V) experiment column after the results show that no arsenic is present in any of the samples.

Results

The As(III) standard elutes from 4 to 18 ml (Fig. 4.2). The MMA analyses show that arsenic is present from 4 to 14 ml, and from 4 to 24 ml for the two different experiments. DMA elutes from 8 to 20 ml (Fig. 4.2). No arsenic from the As(V) standard is observed in any eluent samples between 0 and 40 ml. Therefore, 40 ml of HCl is added

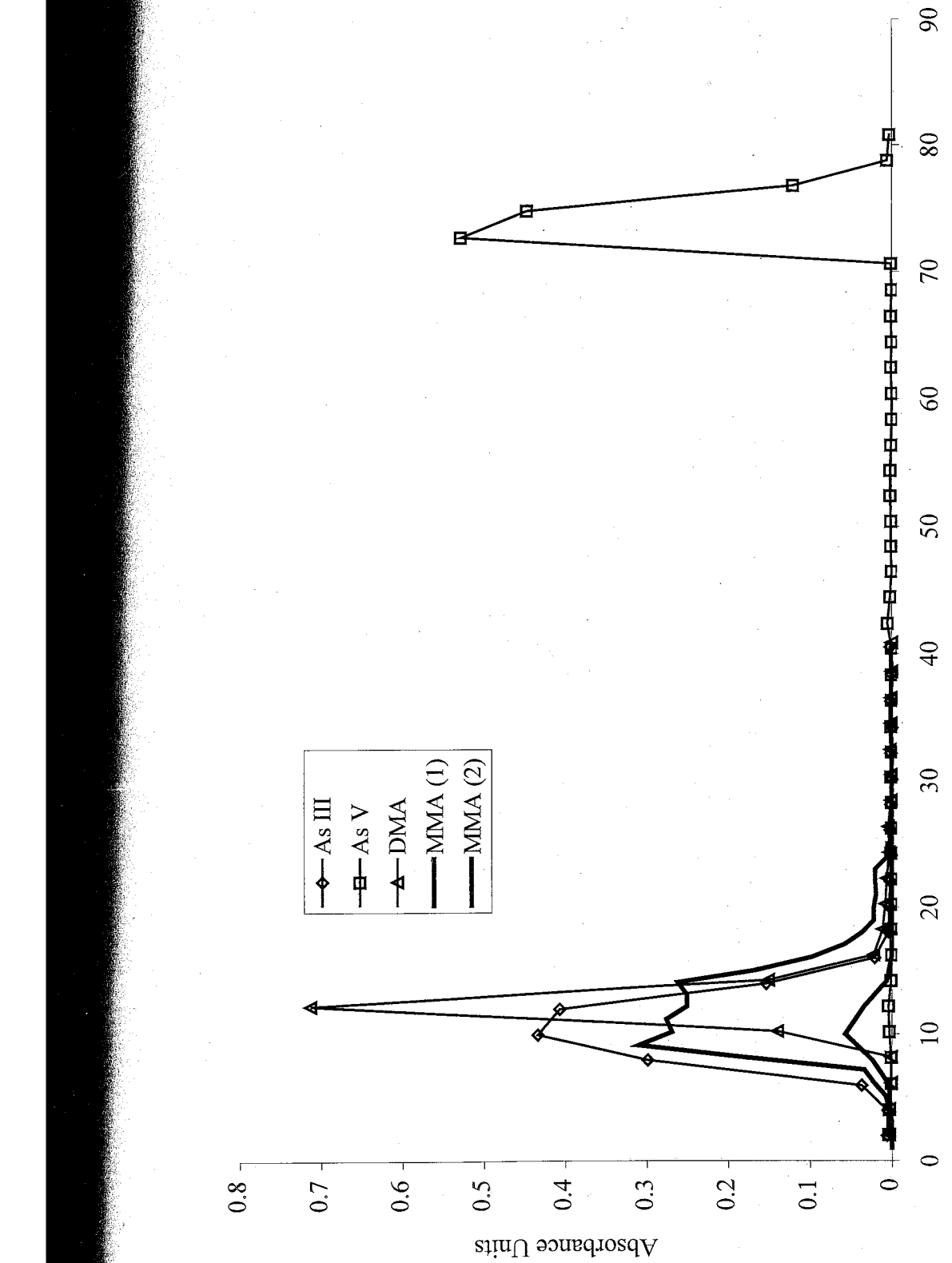


Figure 4.2. Results of the Modified Resin I, showing As(III), As(V), DMA, and MMA breakthrough.

to the As(V) experiment column. The 40 to 80-ml aliquots have arsenic present between 70 and 80 ml. Recoveries data is not available for these analyses.

Discussion and Interpretation

The only modification in these experiments is the pretreatment of the resin. It is shown that As(V) is retained over a larger eluent volume as a result. This increased retention means that separation of As(III) and As(V) is enhanced. MMA and DMA coelutes with As(III). The elution volume between peaks is great enough that no overlap of As(III) and As(V) is observed. It is unclear what the effect of the delayed introduction of the As(V) eluent has on the experiment.

Conclusions

The acetate-form resin has greater selectivity, or sorption, of As(V) than partially converted chloride resin. The qualitative separation of As(III) from As(V) is increased from <2 ml (Fig. 4.1) to 50 ml (Fig. 4.2). MMA and DMA are not separated from As(III). Organic arsenic coelutes with As(III) in both partially and fully converted resin. Therefore, separation of four species is not possible with a column containing either chloride- or acetate-form resin. Absorbance readings are significantly lower for MMA than for any other species, implying that MMA is difficult to analyze by GFAA.

Testing Increased Sample Volume

In the next set of analyses, the sample volume is increased. This is done to determine whether or not separation of As(III) and As(V) is possible with higher sample

volumes. The resin and column configuration used is the same as for the previous set of experiments. A 25-ml 50-µg/l acidified As(V) standard is introduced into a column that is prepared using the batch-method described above. The sample is eluted with 75 ml of 0.12 M HCl. This experiment is repeated for a 50 µg/l, As(III) standard.

Results

The As(V) standard eluted in the 40 to 75 ml range (Fig. 4.3). Arsenic concentrations of 2 µg/l are detected in the 5 to 30 ml range on the As(V) analysis. The recovery is 80%. The As(III) standard elutes in the 0 to 48 ml range (Fig. 4.3). There is some arsenic present in the As(III) run near the detection limit (< 2 µg/l) in the 52-54 ml, 62-64 ml, and 70-76 ml aliquots. As(III) recovery is 106%.

Discussion and Interpretation

The results show that the arsenic species are not completely separated. In the combined plot, both As(III) and As(V) are detected in samples between 40 to 46 ml. Arsenic concentrations are near 2 µg/l in this range. The graph shows that As(III) and As(V) have bell-shaped eluent curves, and that arsenic detection overlaps.

Conclusions

Increasing the sample volume does maintain some separation of the species. It appears that the 0.12 M HCl is responsible for stripping As(V) from the resin, and that As(III) passes through the column regardless of sample volume. The modifications to the method are insufficient to separate As(III) from As(V) completely. To use this method of

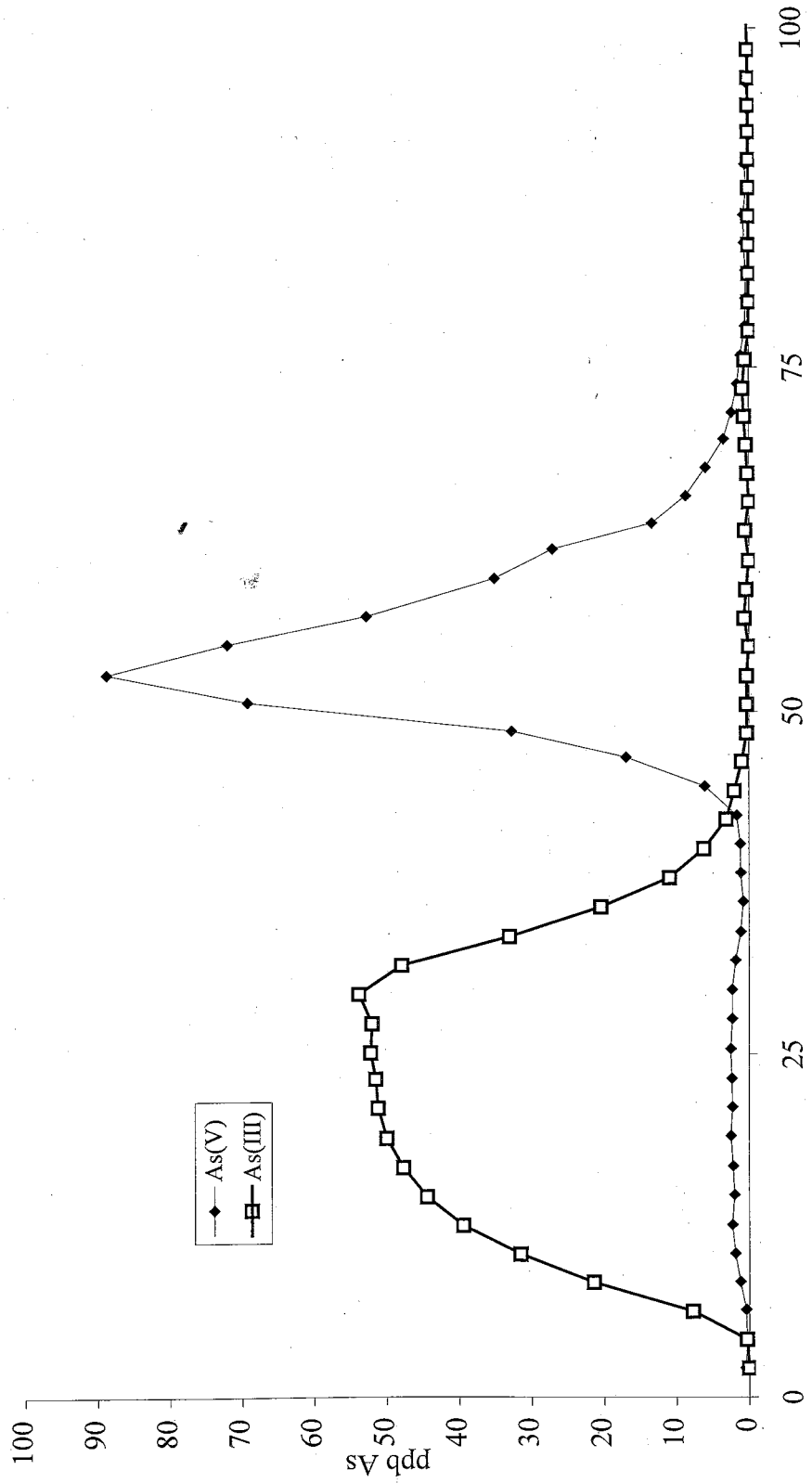


Figure 4.3. Results of Modified Resin II, showing As(III) and As(V) breakthrough.

separation would be to compound the error inherent in the separation. It is shown that resin conversion will retain As(V) in the column, so further investigation of the resin conversion is necessary to separate the species with a distinct gap of eluent that contains no arsenic. There are several factors to consider for improving these analyses. First, the resin may retain As(V) longer if it is treated differently (e.g. greater conversion, different form). Also, a different batch of resin with the same pretreatment may respond differently, and the arsenic species may elute in a different volume range.

Testing the New Resin

The goal of these analyses is to see if the larger sample volume can be used and still produce good recoveries and peak separation. Resin treatment is again investigated. An untreated sample of resin is batch-converted as described in the Methods section under Ion Exchange Resins (p. 41). This experiment differs from above experiments only in that a different batch of resin is used, with different manufacturer lot numbers and from a different bottle. A 25-ml, 20 µg/l As(V) standard is introduced into the column, this analysis is repeated for As(III).

Results

As(V) eluted in the 60 to 86 ml range (Fig. 4.4) with a recovery of 79%. There is some arsenic present in each aliquot between 0 and 24 mls, but each of those aliquots had a concentration lower than 2 µg/l. The As(III) standard eluted from 0 to 44 ml (Fig. 4.4) with a recovery of 106%. There is some arsenic present in the aliquots from 62 to 76 ml, but concentrations are lower than 2 µg/l.

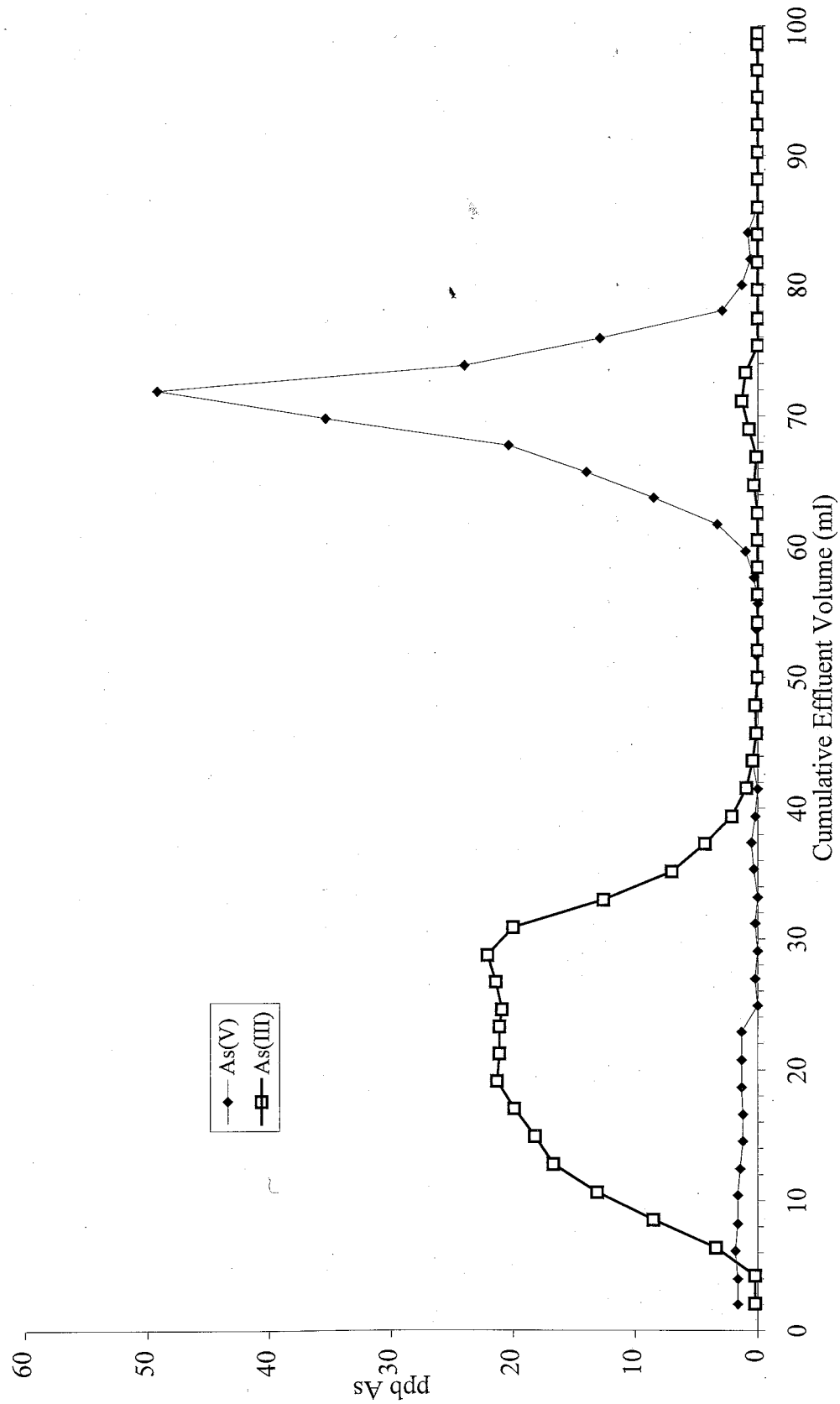


Figure 4.4. New Batch of Resin, showing As(III) and As(V) breakthrough at 20 ppb.

Discussion and Interpretation

There is qualitative separation of As(III) and As(V). The detection of 0.2 to 2.8 µg/l arsenic in the 62 to 76 ml range in the As(III) experiment could be background noise or the detection of arsenic due to As(III) oxidation. There is 1.3 to 1.8 µg/l arsenic present in the first 25 ml of As(V) elution. Recovery is 78.6% for As(V) and 106.0% for As(III).

Conclusions

The increased resin conversion had a direct correlation to the separation of As(III) from As(V). The aliquots from 44 to 60 ml contain no measurable arsenic in either run. As(V) began to elute at 40 ml in the previous set of analyses, and at 60 ml in this set of experiments (Figs. 4.3 and 4.4). The experiments show both used resins converted to acetate-form according to BioRad recommendations. Because the conversion from chloride- to acetate-form resin are experimentally the same, each batch of resin converted should be checked with an As(V) standard prior to use.

Testing of Arsenic Speciation at Low Levels

To be of commercial interest, the method of arsenic separation must work at total concentrations of ≤ 10 µg/l. Previous experiments used arsenic standards that are in the 20 to 100 µg/l range. A 25 ml, 5 µg/l As(V) standard is introduced in a fresh acetate resin column and eluted with 75 ml 0.12 M HCl, as previous experiments. The experiment is repeated for a 5 µg/l As(III) standard.

Results

The As(V) standard eluted from 54 to 80 ml (Fig. 4.5). Recovery for this experiment is 96%. The As(III) standard eluted in the 0 to 46 ml range (Fig. 4.5) with a recovery of 104%. Some arsenic is shown in the aliquots between 66 and 78 ml.

Discussion and Interpretation

Both species are quantitatively separated. Some arsenic is present in the 66 to 78 ml range for the As(III) experiment, which is likely due to oxidation of As(III) to As(V).

Conclusions

The introduction of arsenic species in concentrations lower than 20 μg/l show that As(III) is separated from As(V) just as well as in experiments using arsenic concentrations ≥ 20 μg/l. The recoveries do not appear to be much different from recoveries from other experiments.

Cumulative Error Analysis of ASK2 Runs

Forty-seven separate ASK2 runs that capture eluent in ~2-ml aliquots are combined for comparative and statistical data analysis. Twenty-nine are single species As(V) runs, 18 are single species As(III) runs. The concentration and species of the arsenic standards and % recoveries are shown in Table 4.1, with a reference to the run title so that complete data associated with each run, including eluent masses, calibration, and recovery statistics, can be easily found in Appendix A.

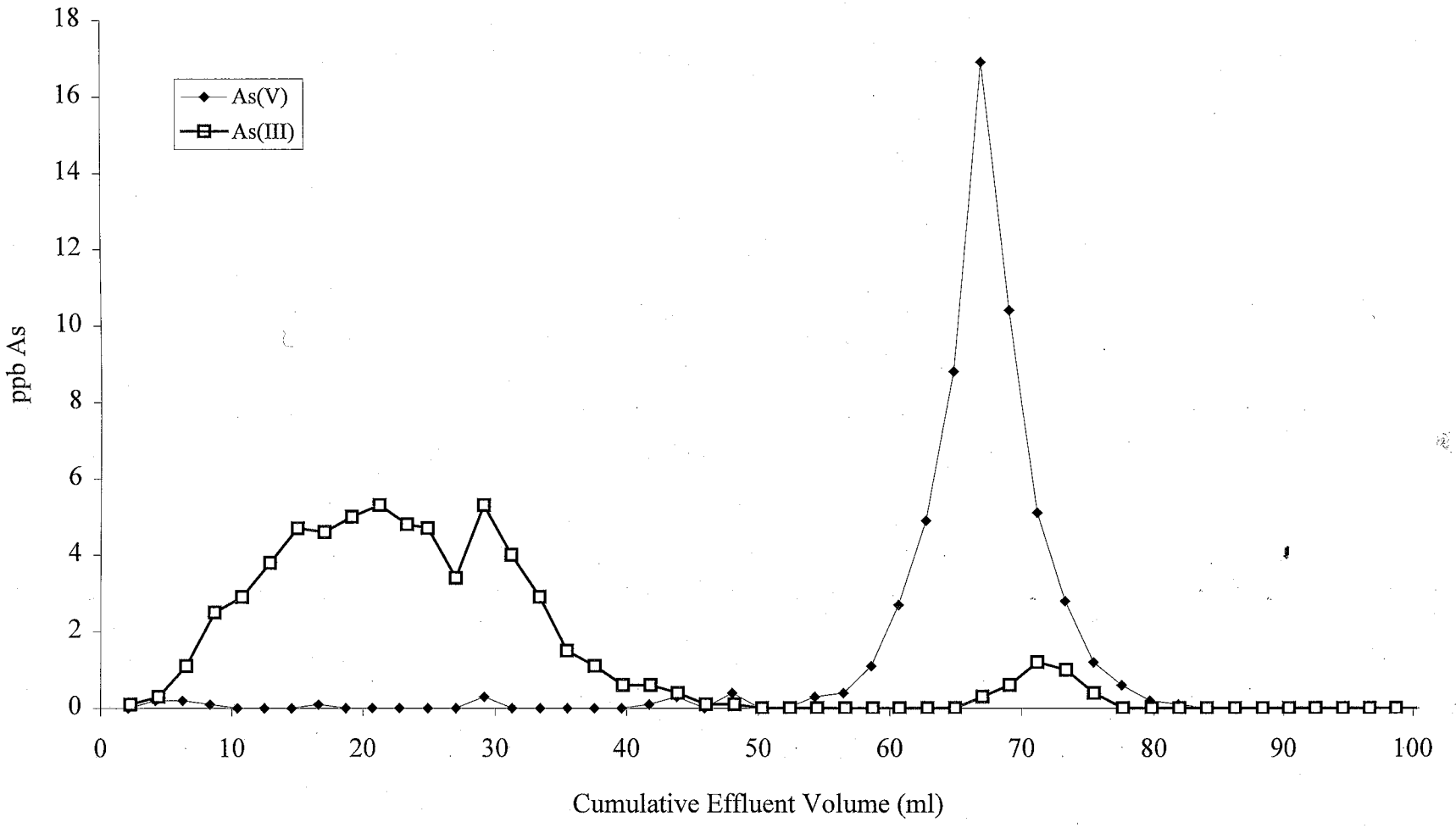


Figure 4.5. Low Level Arsenic Experiments, showing As(III) and As(V) breakthrough at 5 ppb.

Results

Table 4.1. Species, concentration in µg/l, recovery, mean recovery, and analysis number data for ASK2 analyses that capture the eluent in 2-ml aliquots.

Species	µg/l	% Recov.	Mean	Analysis No.	Species	µg/l	% Recov.	Mean	Analysis No.
As(V)	2	144.62		090299B	As(III)	2	131.88		092499D
As(V)	2	126.88		090399A	As(III)	2	127.93		092499E
As(V)	2	108.93		090399B	As(III)	2	109.64		092499F
As(V)	5	87.28		082999B				123.2±11.9	
			126.8±17.8		As(III)	5	111.18		092399A
As(V)	5	96.39		090799C	As(III)	5	104.44		092399B
As(V)	5	125.44		082399B	As(III)	5	114.10		092399C
As(V)	5	87.89		082899C				109.9±5.0	
			99.2±17.9		As(III)	10	87.23		091699A
As(V)	10	88.40		082799B	As(III)	10	127.35		091699B
As(V)	10	90.85		082799C	As(III)	10	140.35		091699C
As(V)	10	107.56		090199C				118.3±10.0	
As(V)	10	82.10		090799B	As(III)	20	125.66		091199D
			92.2±10.9		As(II)	20	112.82		091199E
As(V)	20	73.80		090799A	As(III)	20	106.02		091199F
As(V)	20	92.19		090199B				114.8±10.0	
As(V)	20	77.83		082499A	As(III)	50	106.61		091199A
As(V)	20	100.14		082699A	As(III)	50	114.95		091199B
			86.0±12.3		As(III)	50	121.17		091199C
As(V)	50	78.18		082399A				114.2±7.3	
As(V)	50	60.32		083199A	As(III)	100	104.88		092499C
As(V)	50	65.74		083199B	As(III)	100	105.94		092499B
As(V)	50	82.97		090199A	As(III)	100	104.67		092499A
As(V)	50	78.40		090299A				105.2±0.7	
As(V)	50	81.29		090999A	As(III)			114.3±12.7	
As(V)	50	78.49		090999B					
As(V)	50	92.65		090999C					
As(V)	50	78.18		082399A					
As(V)	50	80.71		082899D					
As(V)	50	77.19		082999A					
			77.6±8.5						
As(V)	100	85.31		082799A					
As(V)	100	86.66		082899A					
As(V)	100	81.11		090799D					
			84.4±2.9						
As(V)			90±18.3						

Discussion and Interpretation

There is a difference between recoveries for As(V) species vs. As(III) species. The As(III) species consistently yields a higher recovery than the As(V) species at the same standard concentration. All species are standardized using an As(V) standard, and it

is possible that the GFAA will always report an As(III) standard of the same concentrations as higher in concentration than an As(V) standard. Another possible explanation of greater As(III) recoveries than As(V) recoveries may be that As(V) is not stripped from the resin completely, while As(III) passes through the resin without significant retention. This explanation is less likely, because mean As(III) recoveries are greater than 100%, while mean As(V) recoveries are mostly below 100%. Therefore, a difference in detection of arsenic by the GFAA is the most likely cause of increased As(III) recoveries over As(V) recoveries.

As the concentration of the standard increases from 2 µg/l to 100 µg/l, the recovery decreases. This is possibly because concentrations are so close to the detection limit, that no distinction between background zero values and low level (< 1 µg/l) concentrations can be made. As the arsenic standard concentration decreases, the concentrations being analyzed on the GFAA decrease. Even though the eluent in captured in 2-ml aliquots, it is unlikely that the concentrations in individual sample cups is much higher than the detection limit for most samples. For example, in analysis 090299B (see Appendix A), there are only 5 of 47 samples that have concentrations greater than 2 µg/l. The recovery for only those 5 samples is 77.3%, which means that the remaining 67.3% of the total recovery is derived from samples with concentrations below 2 µg/l. Therefore, a significant amount of the recovery can be derived from samples with arsenic concentrations that are near or below the detection limit, but that are quantified by the GFAA as greater than zero. This type of error is referred to as Type 1 Error: positive detection in a blank.

Conclusions

Mass and concentration errors are expected to be very low, as described in the methods section, while GFAA concentration results have the potential for greatest error. The analysis method consistently over-reports the concentrations of As(III). The analytical technique is also subject to Type 1 Error, and therefore, recoveries increase to above 100% as the analyte concentrations approach the detection limit.

Two-aliquot Laboratory Validation of the ASK2 Method

A simple field portable arsenic speciation method is the overall goal of the investigation. Therefore, the potential differences in the elutions had to be investigated comparing 2-ml aliquot samples to single-species (50-ml) samples. A spiked sample volume of 25 ml is introduced in the column and eluted, followed by 75 ml of 0.12 M HCl. The eluent is captured in two aliquots, the first from 0-50 ml, the second from 50-100 ml. This experiment is performed for 12 As(III) and 22 As(V) standards that ranged in concentration from 2 to 500 µg/l. Five of the analyses contained a mixed standard. The recoveries for each species are reported separately. In addition, four blanks are analyzed. Both aliquots of the ASK2 elution are captured in all runs and analyzed for arsenic. None of the blank samples contained measurable amounts of arsenic, and recoveries are reported as "0" for these analyses.

Results

Table 4.2. Species, concentration, recovery, mean recovery, and analysis number data for ASK2 analyses that capture the eluent in two aliquots.

Species	conc.	% Recov.	Mean	Analysis No.	Species	conc.	% Recov.	Mean	Analysis No.
As(V)	5	104		081799A	As(III)	5	168		081799A
As(V)	5	100		21000	As(III)	5	104		21000
As(V)	5	100		21000	As(III)	5	100		21000
			101.3±23					124.0±38.	
As(V)	10	116		081799B	As(III)	10	78		081799B
			114		As(III)	10	88		081799C
As(V)	20	165		081799C				83.0±7.1	
As(V)	20	58		100799A	As(III)	25	95.2		081799D
As(V)	20	54		100199F				95.2	
As(V)	20	69		100199G	As(III)	50	108.4		081799E
As(V)	20	72		100199H	As(III)	50	81.2		21000
As(V)	20	68		100199I	As(III)	50	80.4		21000
As(V)	20	66		100199J				90.0±15.9	
			78.9±38.5		As(III)	500	94		21000
As(V)	25	95		081799D	As(III)	500	97.6		21000
			95		As(III)	500	90.8		21000
As(V)	50	116		081799E				94.3± 3.4	
As(V)	50	66		100199A	As(III)			98.8±23.8	
As(V)	50	59		100199B		blank	0		110999A
As(V)	50	64		100199C		blank	0		110999B
As(V)	50	55		100199D		blank	0		110999C
As(V)	50	57		100199E		blank	0		110999D
As(V)	50	64		21000					
As(V)	50	60		21000					
			67.5±19.8						
As(V)	500	39		21000					
As(V)	500	46		21000					
			42.2±4.8						
As(V)			78.3±29.7						

The mean recovery for all As(III) samples is 98.8±23.8%. The mean recovery for all As(V) samples is 78.3±29.7%. Several of the analyses had very poor recoveries. These analyses are what prompted the run of standards that are shown in the Actual GFAA Error section of the Methods chapter (p. 53-54).

Discussion and Interpretation

The recoveries generally increase to greater than the introduced mass of arsenic when the concentration of the sample approaches the detection limit. Capturing the eluent in two aliquots rather than 50 aliquots has little effect on the accuracy. The recoveries of As(V) are consistently lower than the recoveries of As(III). This trend is observed when many more samples are collected. Thus, it appears that single-species eluent captures do not differ substantially based on elution speed.

Conclusions

Arsenic(V) recovery is consistently lower than As(III) recovery, which is overestimated. The detection method likely overestimates As(III), and the error is not due to a hidden source of arsenic (e.g. in the resin or eluent). The modification of the resin controls the elution point of the species and the time it takes to elute 50 aliquots vs. 2 aliquots does not affect separation.

Field Testing the ASK2 Method Using New Resin

For field sampling, a fresh batch of resin is converted to acetate-form and checked for complete conversion using $AgNO_3$. Cl^- complexed with Ag^+, so the resin conversion method is repeated. The resin is labeled "Super Converted" to indicate that it had been converted twice. Two ASK2 columns are packed into a toolbox with a 50-ml and 25-ml graduated cylinder, a 30-ml dropper-bottle of 10% sulfuric acid to acidify the sample, a 50-ml syringe with a disposable 0.45μm filter tip, several 30-ml sample cups, two 60-ml,

and two 1-l acid-washed Nalgene sample bottles. Socorro and Sedillo Springs are sampled using the field sampling procedure described in the methodology (p. 55-56).

Results

The filtered, acidified arsenic total sample and both speciation samples are analyzed for arsenic. The arsenic total samples contained an arsenic concentration of 35 +/-3 and 36 +/- 3 µg/l for Socorro and Sedillo Spring, respectively. Neither aliquot from the ASK kit (ASK2#1, which contains As(III), or ASK2#2, which contains As(V)) contains measurable arsenic. Two columns are built using the same batch of resin that is used for field sampling. A 25-ml As(V) standard is introduced into the column and eluted with 175 ml, 0.12 M HCl, captured in successive 5-ml aliquots. No arsenic is present in aliquots from 0 to 100 ml, while eluent in the 100 to 150 ml range contains the arsenic. Later experiments in the lab show that As(V) elutes from 100 to 150 ml using the "super converted" resin.

Discussion and Interpretation

There are several explanations for the "blank" ASK2 samples. First, ion interferences didn't allow arsenic that is stripped from the column be detected on the GFAA. This explanation is unlikely the case, because the acidified, filtered sample contained arsenic. Second, the resin conversion could have held As(V) over a larger eluent volume than anticipated from previous results. It is most likely that the resin conversion retained As(V) and it is still present on the column, just as the increased resin conversion enhanced As(III) and As(V) separation in the initial results (Figs. 4.1, 4.2, and

4.3). The interpretation is that since As(III) does not sorb to the resin, and no arsenic is present in either ASK2 aliquot, all arsenic from the samples is As(V). The sites are resampled later to test this theory.

Conclusions

It appears that arsenic speciation is most sensitive to resin-form. The portability of the columns and all necessary equipment is sufficient for field use. Further ASK2 field testing is necessary to determine what ion interferences are present, if any.

Development of the ASK4 Method

The development of the ASK4 kit is based on the ion-exchange method described by Grabinski (1981), which is described in the previous chapter. The goal of these analyses is to see if As(III), As(V), MMA, and DMA could be separated qualitatively and quantitatively. One hundred and sixty batches of analyses are performed in the ASK4 stage of the investigation. Analyses representative of the evolution of our modifications to the method are chosen here for detailed discussion. Results for all analyses performed in this investigation are shown in Appendix B, selected figures are shown here.

Testing, Modification and Discussion of the Grabinski Method

Work begun by Miller shows that As(V) is eluting in the range of DMA. This occurrence of what we termed the "late arsenic" problem is observed both under field and laboratory conditions by Miller, which is verified here. The first experiments replicate the

work published by Grabinski (1981). The first step is to build anion and cation exchange resin columns as described by Grabinski. The columns are not pressurized using N_2 gas. Rather, flow through the columns is gravity driven. To eliminate mixing of the resins, two separate columns are linked together rather than using a single column. The lower column, 10 cm long, contained the anion resin held in place by two frits on either end. The anion column is connected to the cation column by a luer fitting as in Fig. 3.1.

Initial testing focused on resolving whether DMA is present in the waters, or whether As(V) is the only species present and a flaw in the elution sequence or chemistry could eliminate the false peak. A representative analysis is shown in Fig. 4.6. This elution used Grabinski's eluents and their concentrations, showing that arsenic is present in the 130 to 140 ml range, where DMA should have been present. Recovery for this analysis is 113%.

The introduced spike is a laboratory standard and should contain no contaminants. It should therefore be >98% pure, with the possibility of interconversion to As(III), which is not likely. To assure that no organic arsenic is present, the As(V) standard is digested in H_2O_2, boiled for an hour, and brought back to volume with RO water. The results from subsequent experiments continued to show the "late" peak of arsenic in the DMA range (Fig. 4.7) that could not be attributed to DMA.

Grabinski postulates the following: As(III) is relatively neutral in the pH's found in most natural waters and will pass through the resin without adhesion in the 0-30 ml range with 0.006 M trichloroacetic acid (TCA) as the eluent. MMA has a near balanced surface charge with a minor affinity for cation resin due to the induced dipole, allowing it to sorb to the cation resin with weak affinity. A reduction in pH and addition of hydrogen

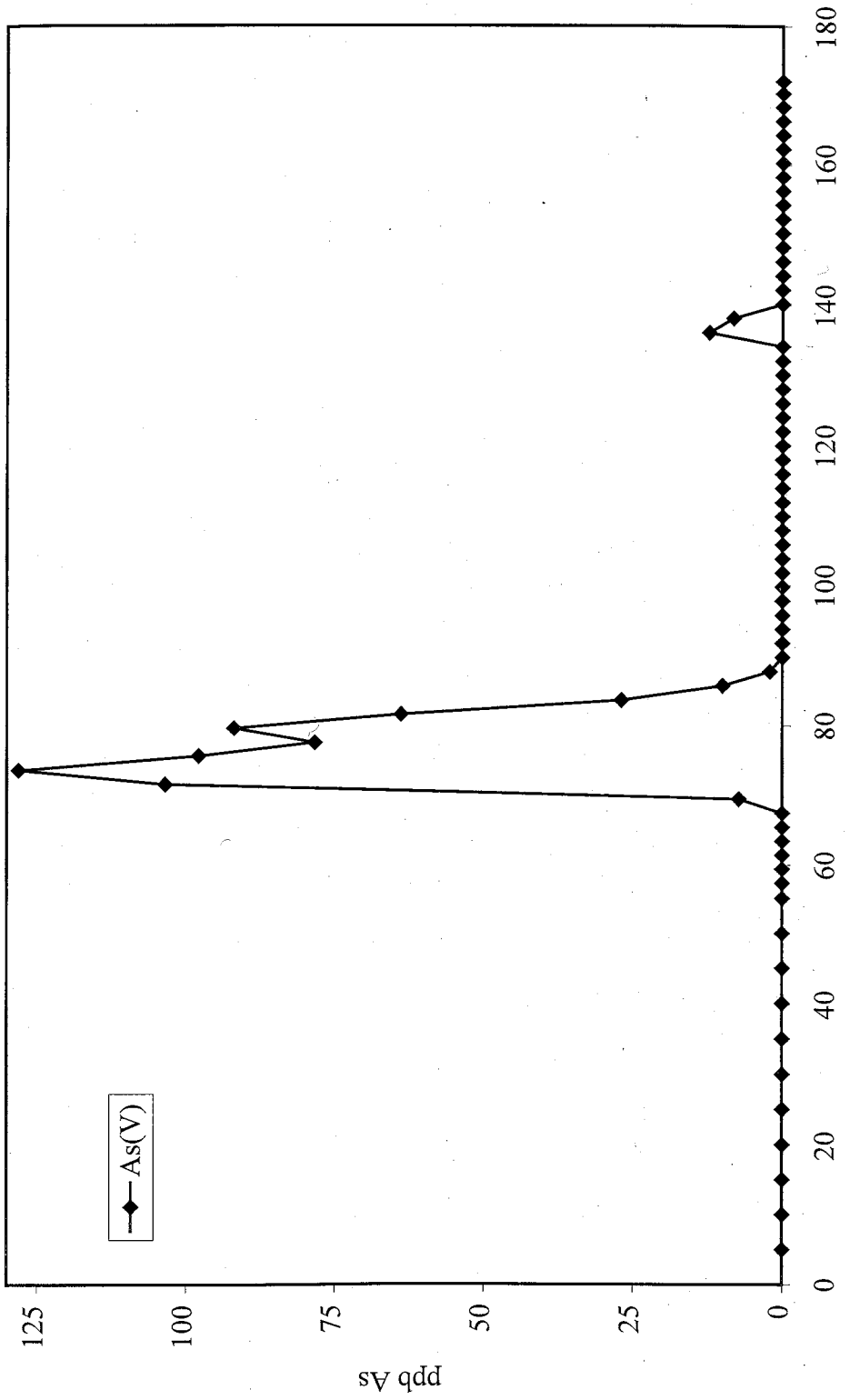


Figure 4.6. Results of the modified Grabinski method showing elution of As(V).

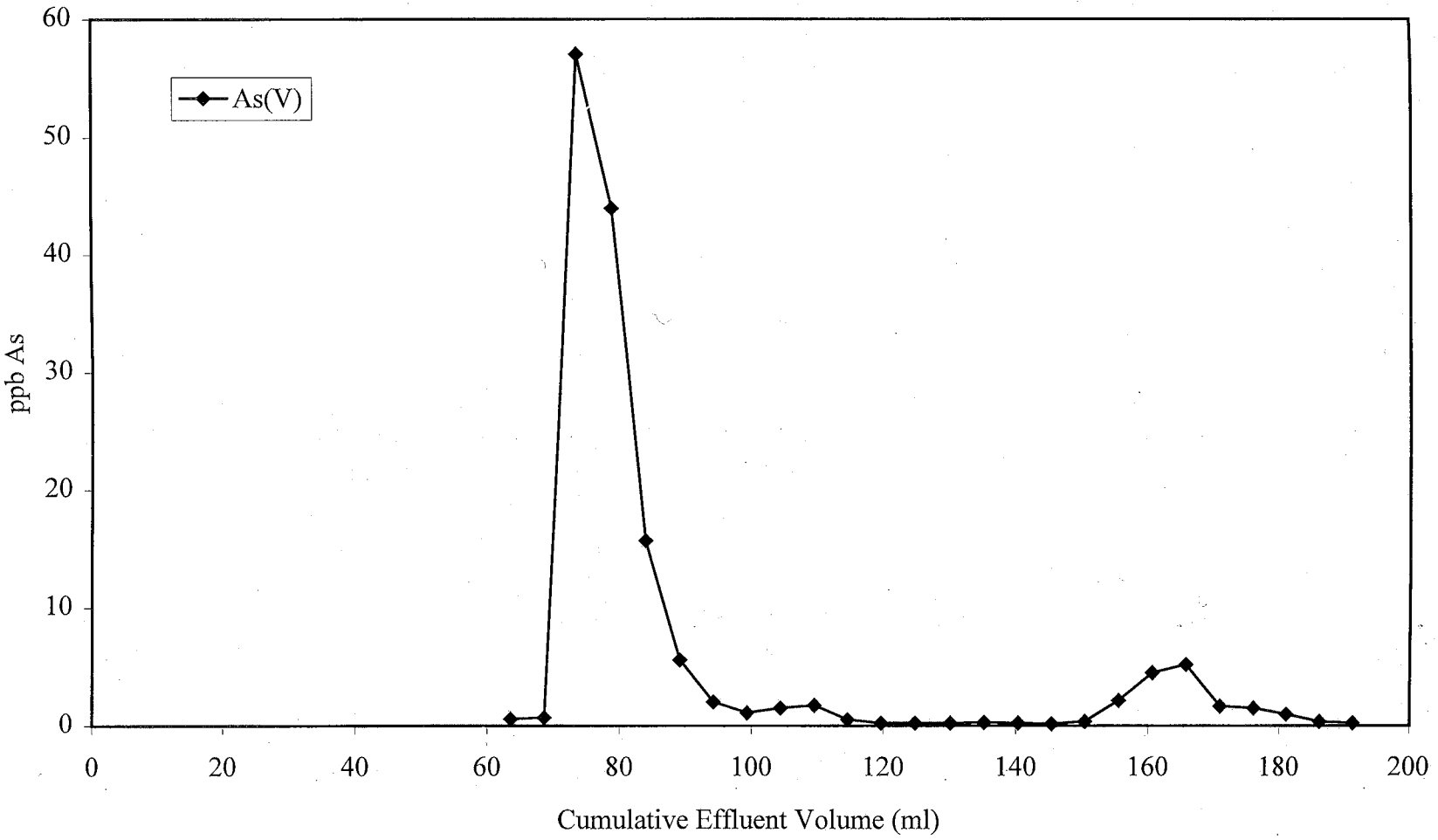


Figure 4.7. ASK4 elution showing digested As(V) elution.

ions to exchange with the MMA species sorbed to the resin allows MMA to be released and eluted from the column. Therefore, the second species to elute from the column is MMA, which elutes from ~ 35-60 ml. As(V) is an oxyanion at low pH and sorbs to the anion resin, and is stripped with the introduction of 0.2 M TCA. DMA is a cation at low pH and thus has a strong affinity for cation resin. The introduction of 1.5 M NH_4OH allows DMA to be displaced onto the anion resin. The final stripping of DMA from the column is done with the addition of 0.2 M TCA, which displaces DMA.

It appears there is insufficient stripping power to remove all As(V) from the resin. This allowed some As(V) to be retained on the anion resin, which is later coeluted with DMA (Fig. 4.6, Fig. 4.7). To resolve how much acid is needed to strip As(V) from the column completely, single cation columns are set up. A 2-ml As(V) sample is eluted with 100 ml of 0.006 M TCA. The results show that arsenic is present until ~25 ml of eluent had passed through the column (Fig. 4.8). Recovery for this experiments is 131%.

To test whether or not the late peak is due the concentration of exchangeable ions, this experiment is repeated using 0.48 M HCl rather than 0.2 M TCA. The eluent volume required to elute As(V) is approximately 25 ml (Fig. 4.9). The mass of arsenic recovered in this experiment is 92%.

Conclusions

The mass recoveries of individual species shown here have high variation, but As(III), MMA, and DMA elute in the predicted ranges. However, As(V) elutes in the As(V) range and elutes trace amounts of arsenic in the DMA range. Thus, As(V) is likely

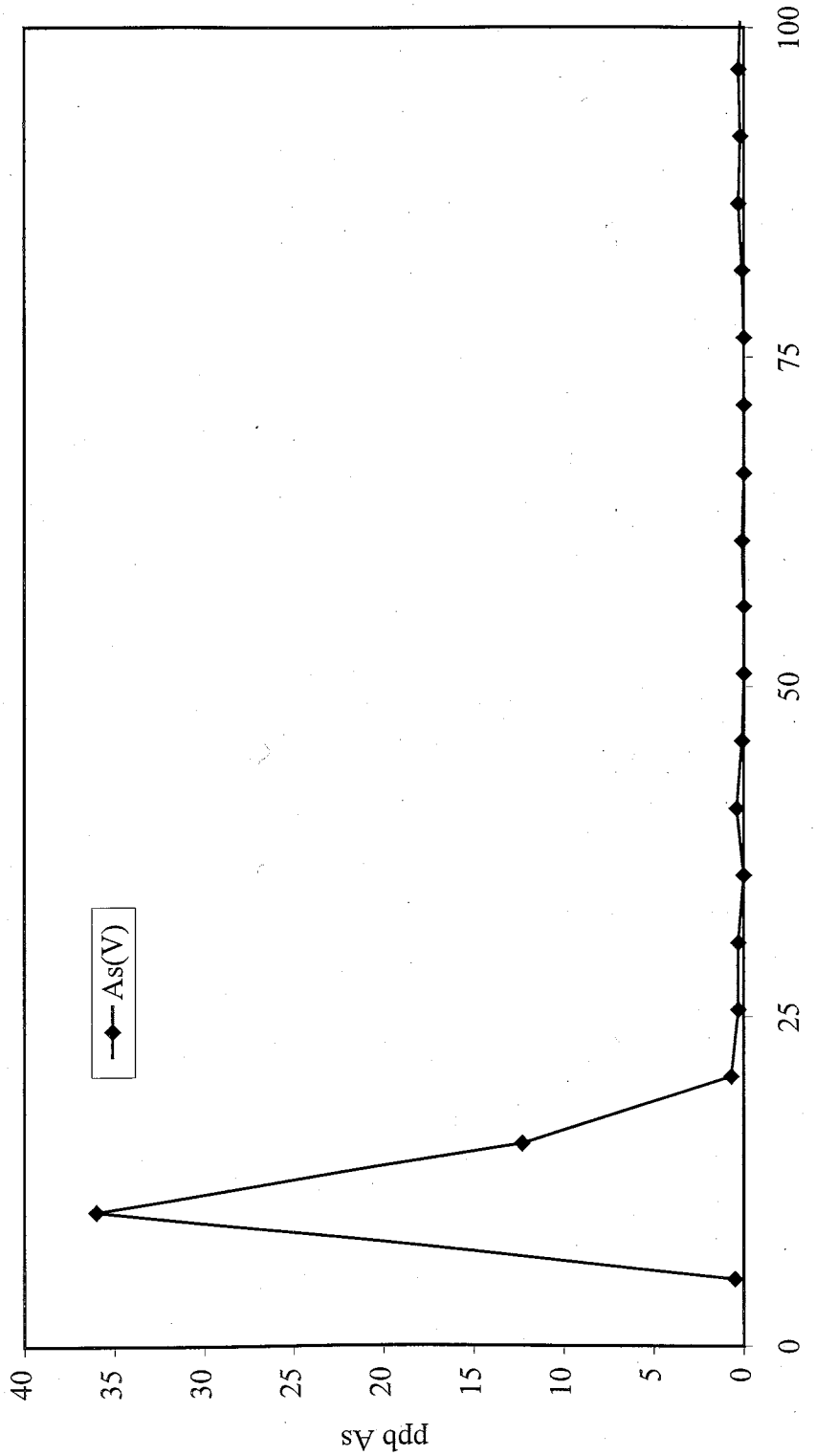


Figure 4.8. ASK4 elution on cation column showing As(V) standard.

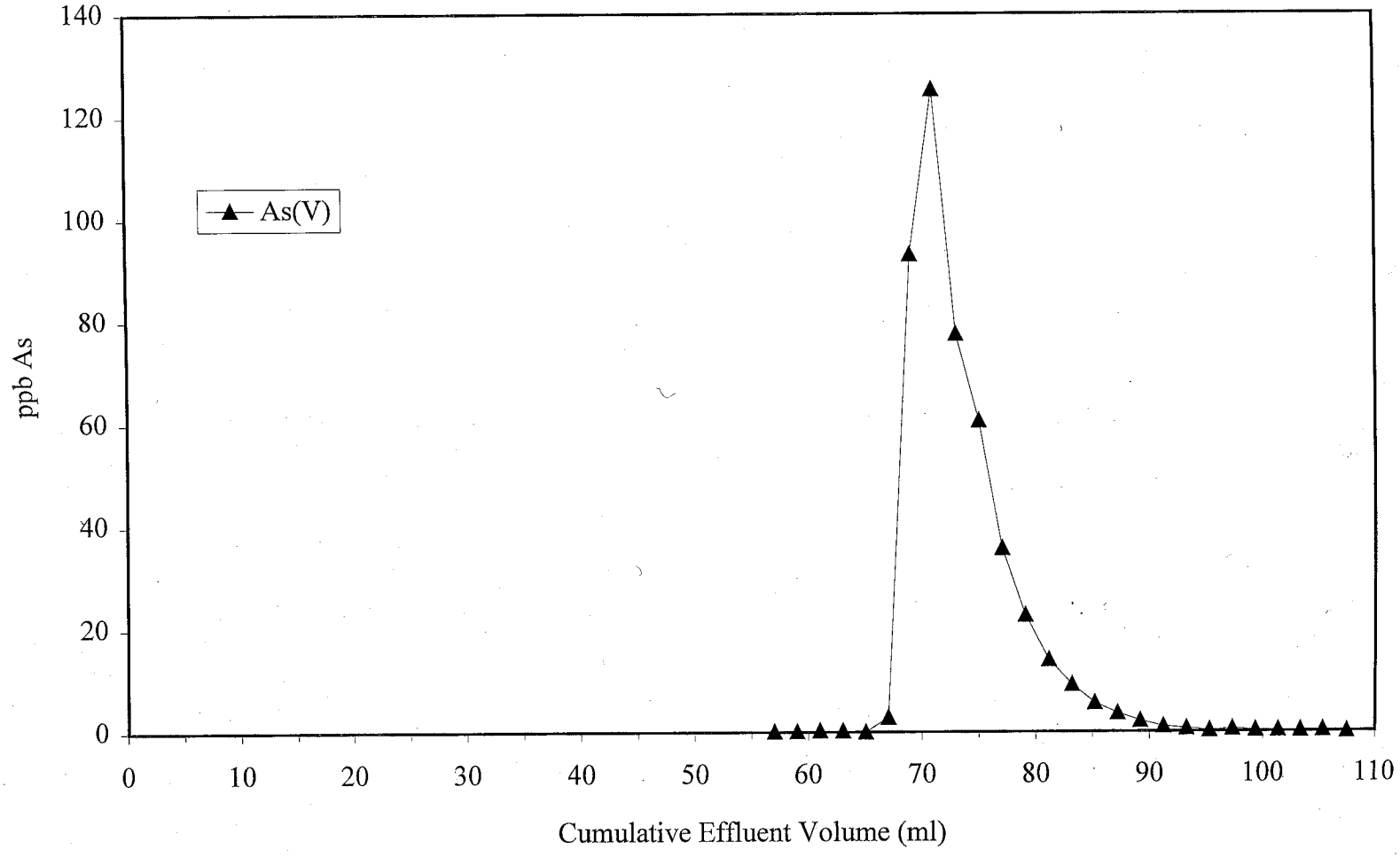


Figure 4.9. ASK4 Analysis showing As(V) elution using HCl as eluent.

underpredicted in quantification, whereas DMA is likely overestimated. There is a possibility that DMA will be reported when it is in fact not present using this method.

Geochemistry and Arsenic Speciation in Four Thermal Areas

Field Sampling

Forty-seven samples are taken from four thermal areas in New Mexico. Results for analyses are grouped by geographic location, yielding four sample sets. Sample locations are shown in Fig. 2.1, a legend for site numbers is shown in Table 2.1. Major and minor ions that are analyzed are listed and the analytical techniques are described in the methods section. Arsenic species are not separated in the Austin well, Intor well, Bosque del Apache Drinking Water well, Hard Luck Crossing, Antelope Well, and Hackberry Well. Anions are not analyzed in the Antelope Well sample. No GPS data are available for the following locations: Bosque del Apache 1NW, Austin, Intor, Hard Luck Crossing, Artesian Well, and Hay-Oh-Kay, but locations are estimated and plotted. The analytical results related to field sampling are shown in Appendix D.

Results from all Field Samples

Combined field sample analyses for major cations (Na^+, Ca^{2+}, and Mg^{2+}) and anions (HCO_3^-, SO_4^{2-}, and Cl^-) are normalized and plotted after Piper (1953) (Fig. 4.10). The thermal waters from Socorro (Nos. 1, 2, 7) cluster in the Na-HCO_3 region of the diagram, while remaining Socorro samples are variably dispersed. Water samples from downtown Truth or Consequences cluster in the sodium-chloride area of the diagram. The two samples from the Bosque that have the highest amounts of arsenic (Nos. 16 and 24) have higher sodium and bicarbonate than other samples in that area.

Legend:

△ Jemez Mountains
+ Socorro
□ Bosque del Apache
⊕ Truth or Consequences

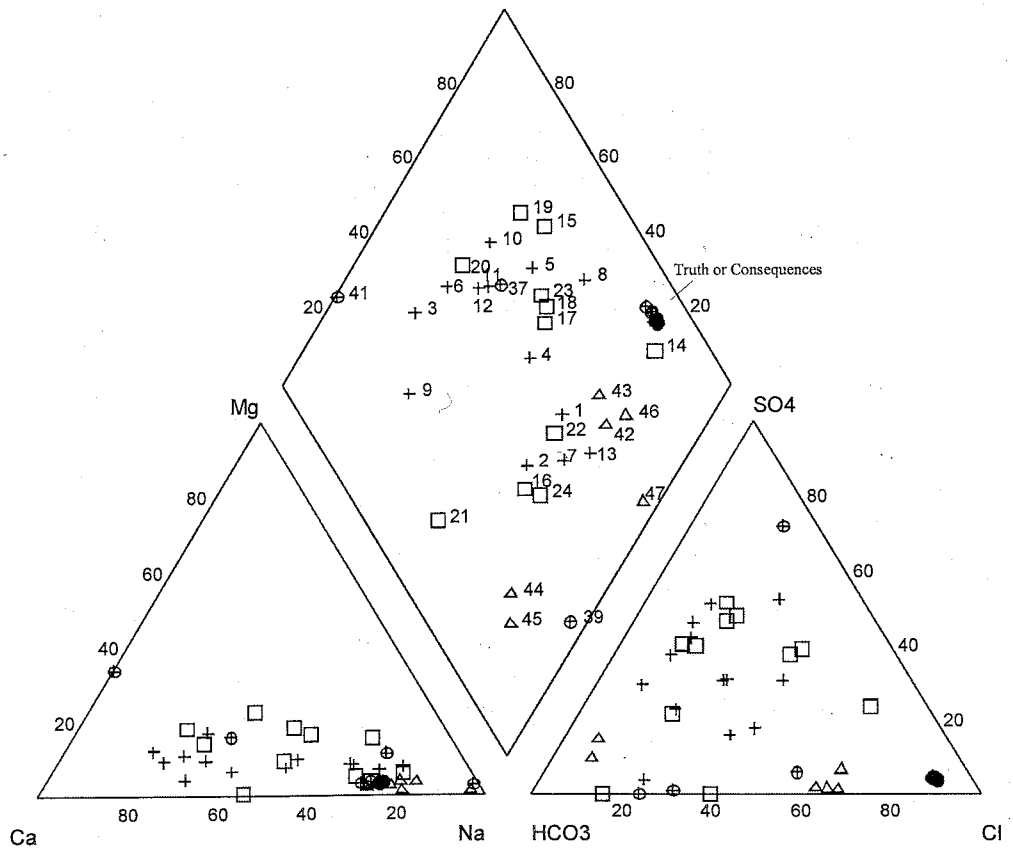


Figure 4.10. Piper Diagram for all Field Samples.

When log chloride is plotted against log arsenic (Fig. 4.11), the Jemez Mountains waters (Nos. 42-47) show a positive linear trend, with an r value of 0.9947. The two populations with the highest chloride are the Truth or Consequences samples (Nos. 25-36) and the Jemez Mountains samples (Nos. 42-47). Their arsenic variation is substantially different. The Truth or Consequences samples have very little arsenic while the Jemez Mountains samples have the highest amount of arsenic of all samples. The Truth or Consequences samples cluster tightly. The Socorro and Bosque samples show no linear covariation. Sedillo Spring has the lowest chloride and Cook Spring has the highest chloride.

When the log silica content of all samples is plotted against log arsenic (Fig. 4.12), the Jemez Mountains samples (Nos. 42-47) have the highest amount of silica and cluster, but show no statistical linear correlation (r=0.959, n=6) when the two springs at Spence (Nos. 44 and 45) are included in the sample group. Jemez Mountains samples exclusionary of the Spence springs samples show a negative arsenic vs. silica correlation (r=0.959, n=4). The Socorro and Bosque del Apache samples do not show a statistical correlation (r=0.1703). The Socorro thermal springs cluster, but do not show statistically meaningful covariation (r=0.1019). The Truth or Consequences samples cluster, but show no statistical correlative trend (r=0.537).

A log-log plot of arsenic vs. TDS (Fig. 4.13) shows two distinct trends. Arsenic correlates positively with TDS in the Jemez Mountains samples (r=0.9911). The thermal waters (Nos. 1, 2, 7) in Socorro show an inverse correlation of arsenic to TDS (r=0.9974), with Cook Spring (No. 7) showing the greatest TDS and lowest As. Samples for the entire Socorro area (n=13) show no linear covariation (r=0.3006). Samples from

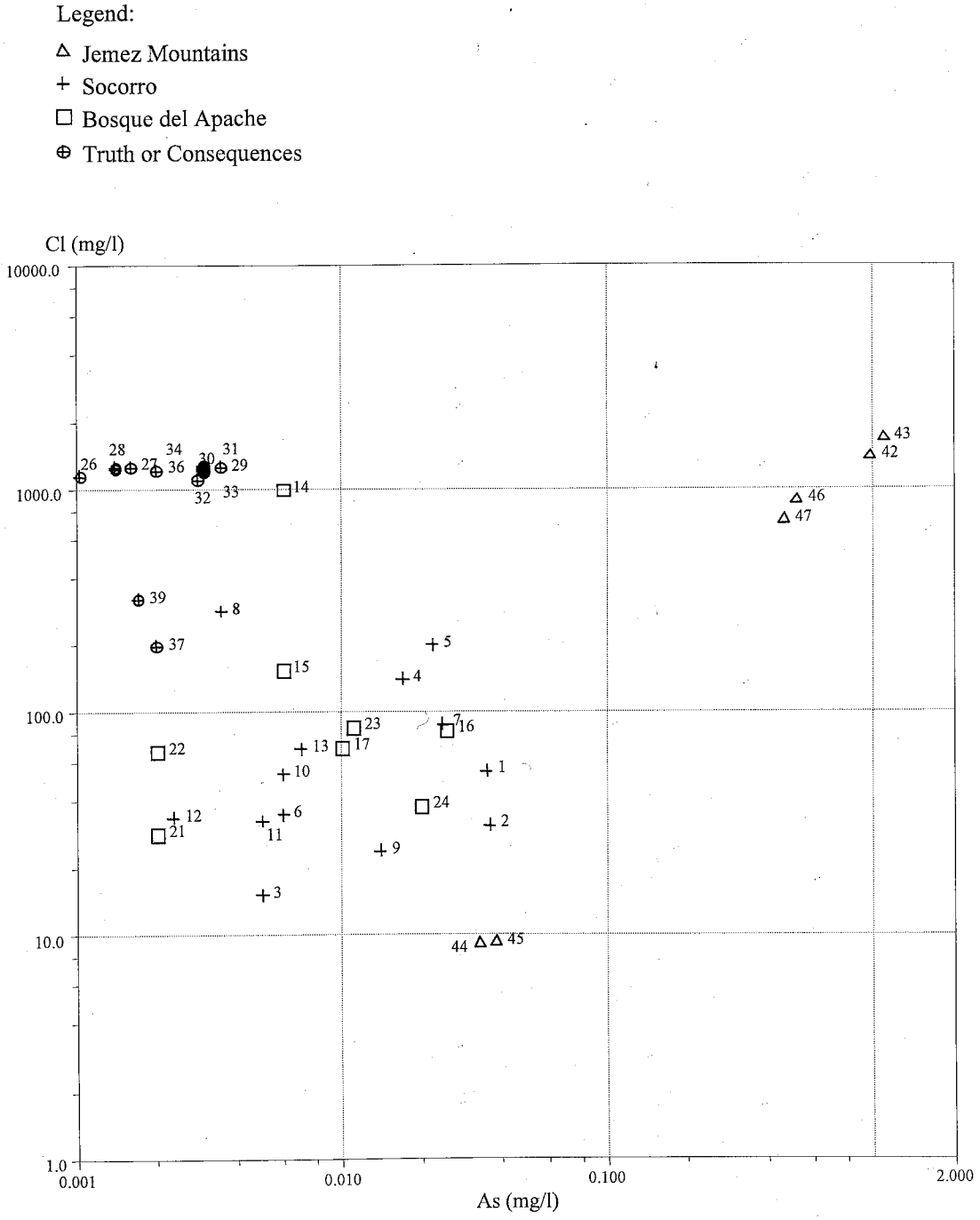


Figure 4.11. Log Arsenic vs. Chloride for all Field Samples.

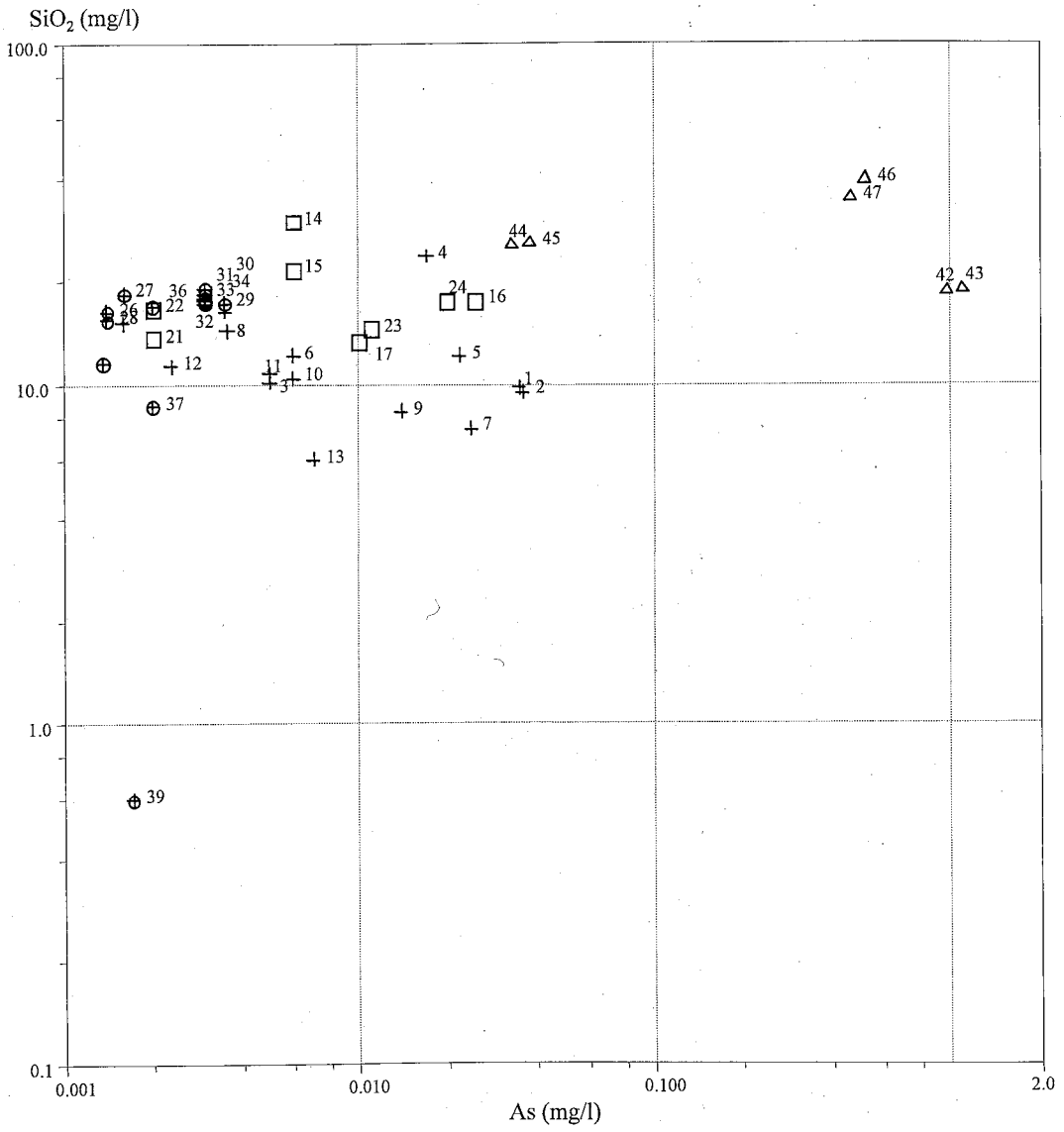


Figure 4.12. Log Arsenic vs. Silica for all Field Samples.

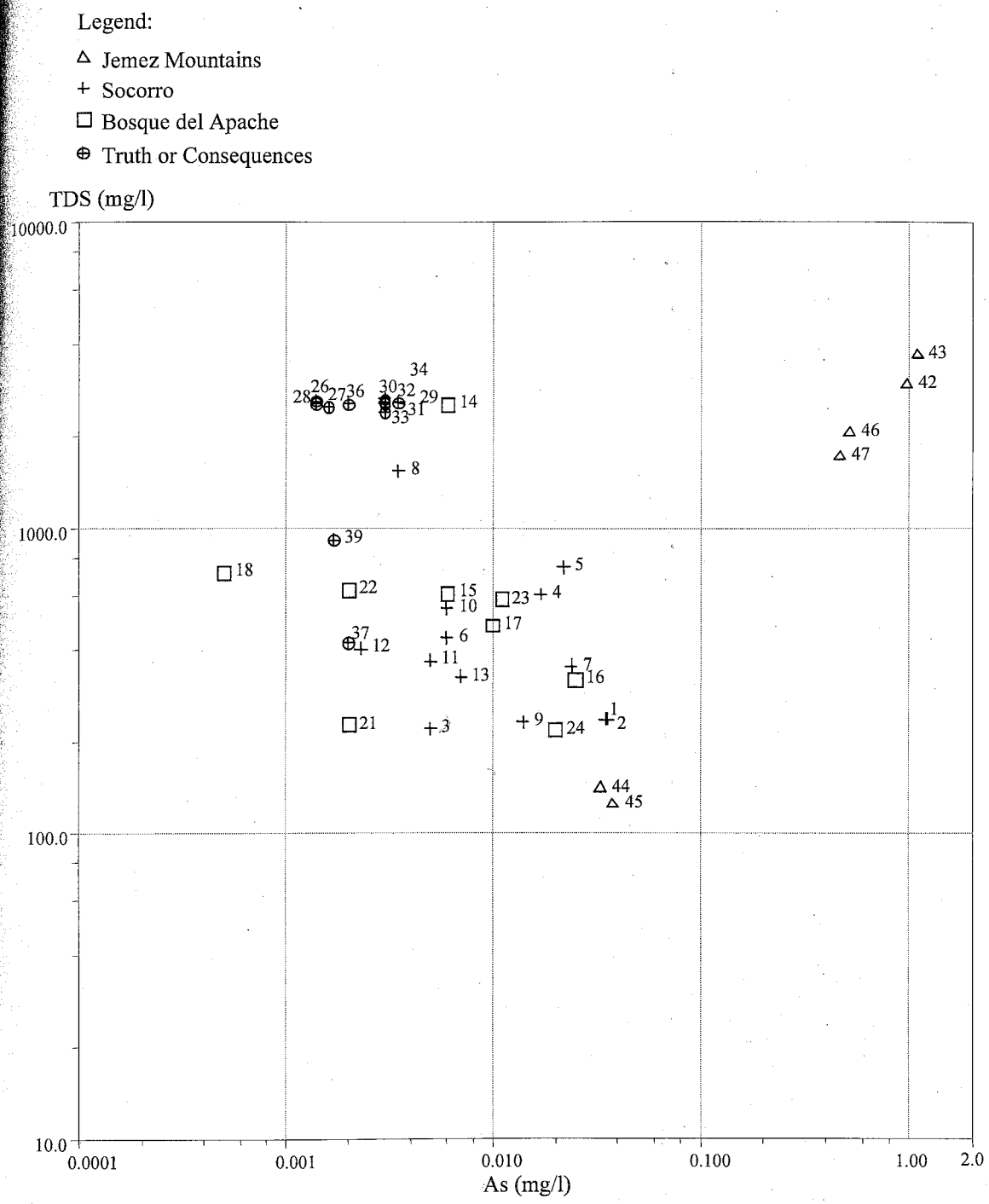


Figure 4.13. Log Arsenic vs. Total Dissolved Solids (TDS) for all Field Samples.

Truth or Consequences (Nos. 25-36) have extremely high TDS and cluster, but show no covariation (r=0.044).

A plot showing pH vs. log arsenic (Fig. 4.14) shows that waters tend to have greater amounts of arsenic in them with increased pH. However, the highest arsenic samples (Nos. 42-47) clustered and had the lowest pH. Obtaining the pH in the high-temperature waters of the Jemez Mountains is subject to great error because the temperatures are too high for the instruments used. The pH and Eh values are taken after the water cooled enough to take a reading. If the pHs are accurate, then there is a difference between samples from the Jemez Mountains and remaining samples.

The Bosque del Apache samples (Nos. 14-24) show a no correlation (r=0.5339) between log Na/K vs. As (Fig. 4.15). The Truth or Consequences samples cluster, and show a slight trend (r=0.5886), but no linear covariation. The Jemez Mountains samples show a statistically negative correlation (r=0.826). When samples from Socorro are analyzed, they show no linear correlation.

A log plot of sulfate vs. arsenic (Fig. 4.16) shows no linear covariation for any sample group. Sulfate concentrations in Jemez Mountains samples (Nos. 42-47) do not differ significantly in sulfate from other samples. Truth or Consequences samples (Nos. 25-36) cluster. Samples from the Bosque del Apache (Nos. 14-24) are highest in sulfate.

Concentrations of iron and manganese are combined and plotted against arsenic (Fig. 4.17). Iron and manganese values fell very near the detection limit for all samples. A positive covariation (r=0.9877) is seen in samples from the Jemez Mountains (Nos. 42-47), which show increasing arsenic concentration in samples that show increased iron and manganese. The Bosque del Apache samples (Nos. 14-24) show a negative arsenic to

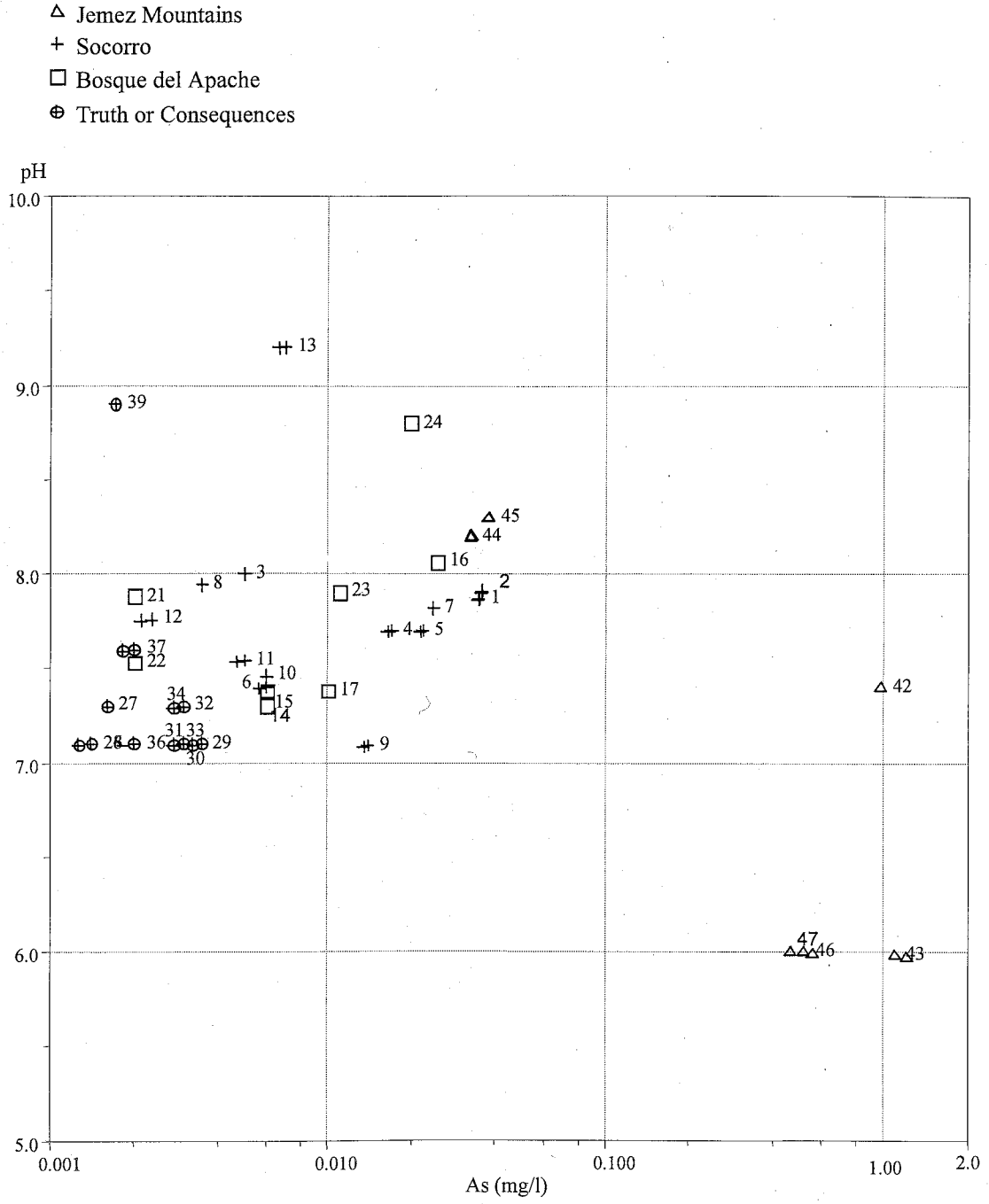


Figure 4.14. Log Arsenic vs. pH for all Field Samples.

Legend:

△ Jemez Mountains
+ Socorro
□ Bosque del Apache
⊕ Truth or Consequences

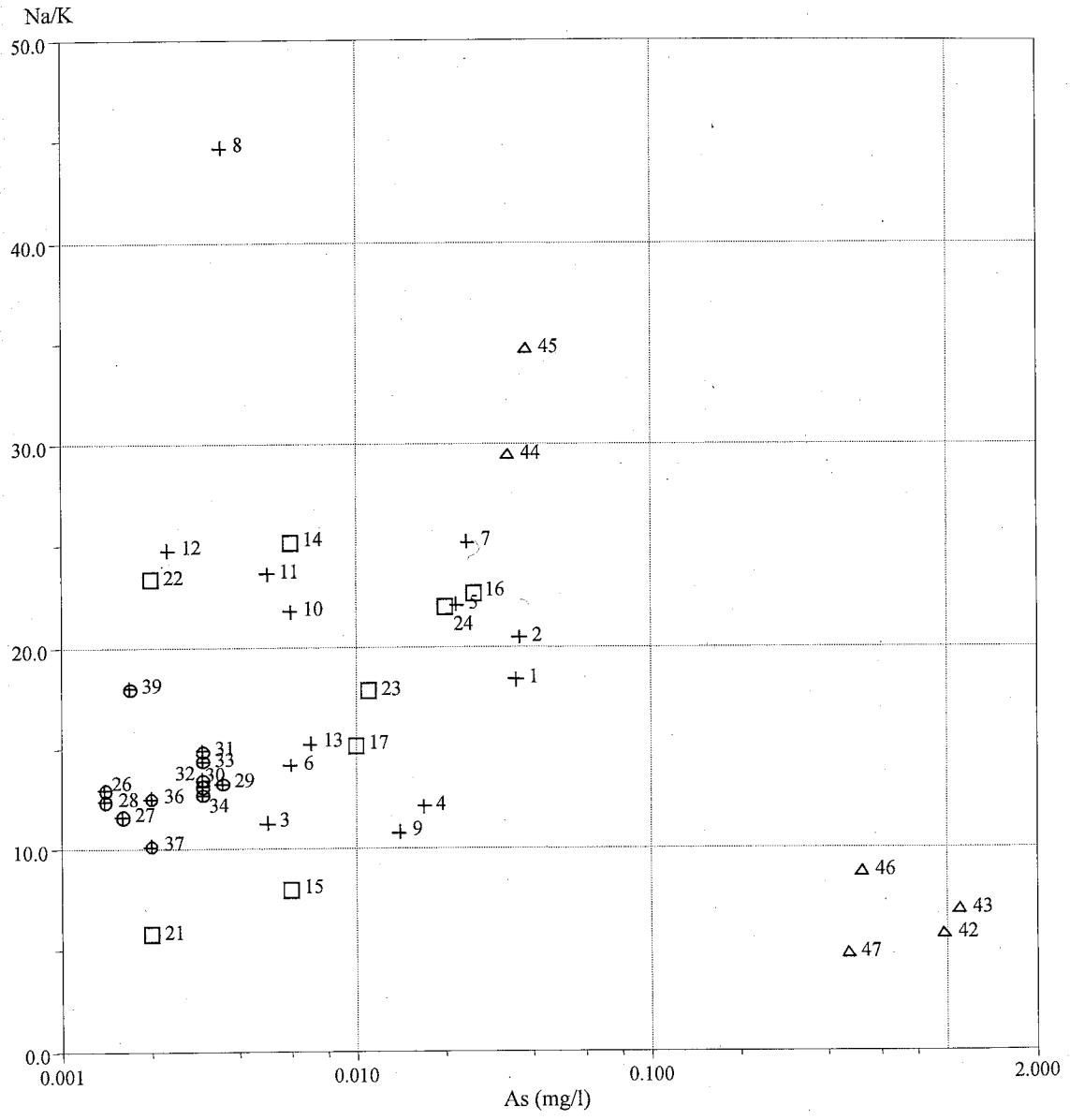


Figure 4.15. Log Arsenic vs. Na/K for all Field Samples.

Legend:

△ Jemez Mountains
+ Socorro
□ Bosque del Apache
⊕ Truth or Consequences

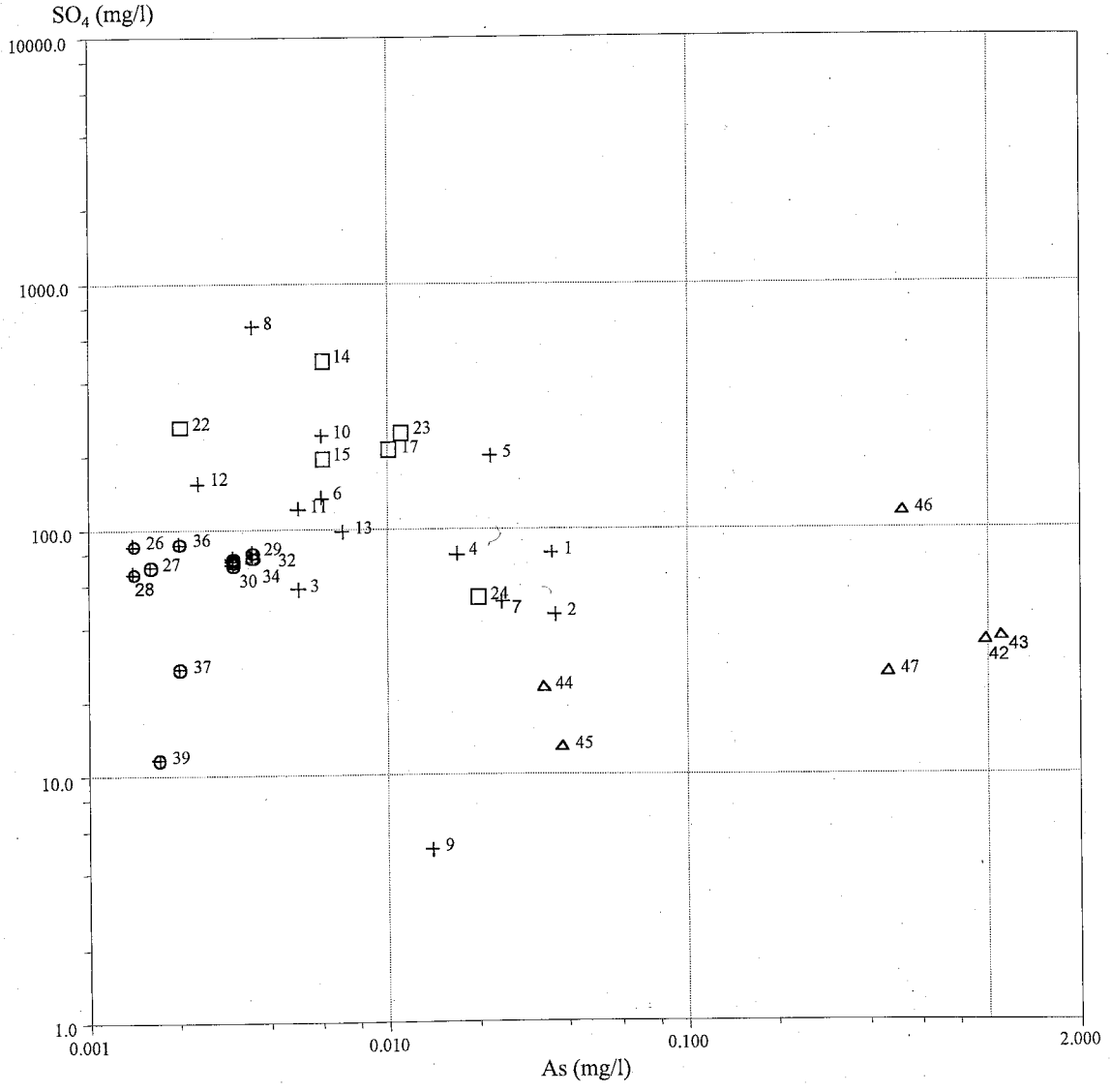


Figure 4.16. Log Arsenic vs. Sulfate for all Field Samples.

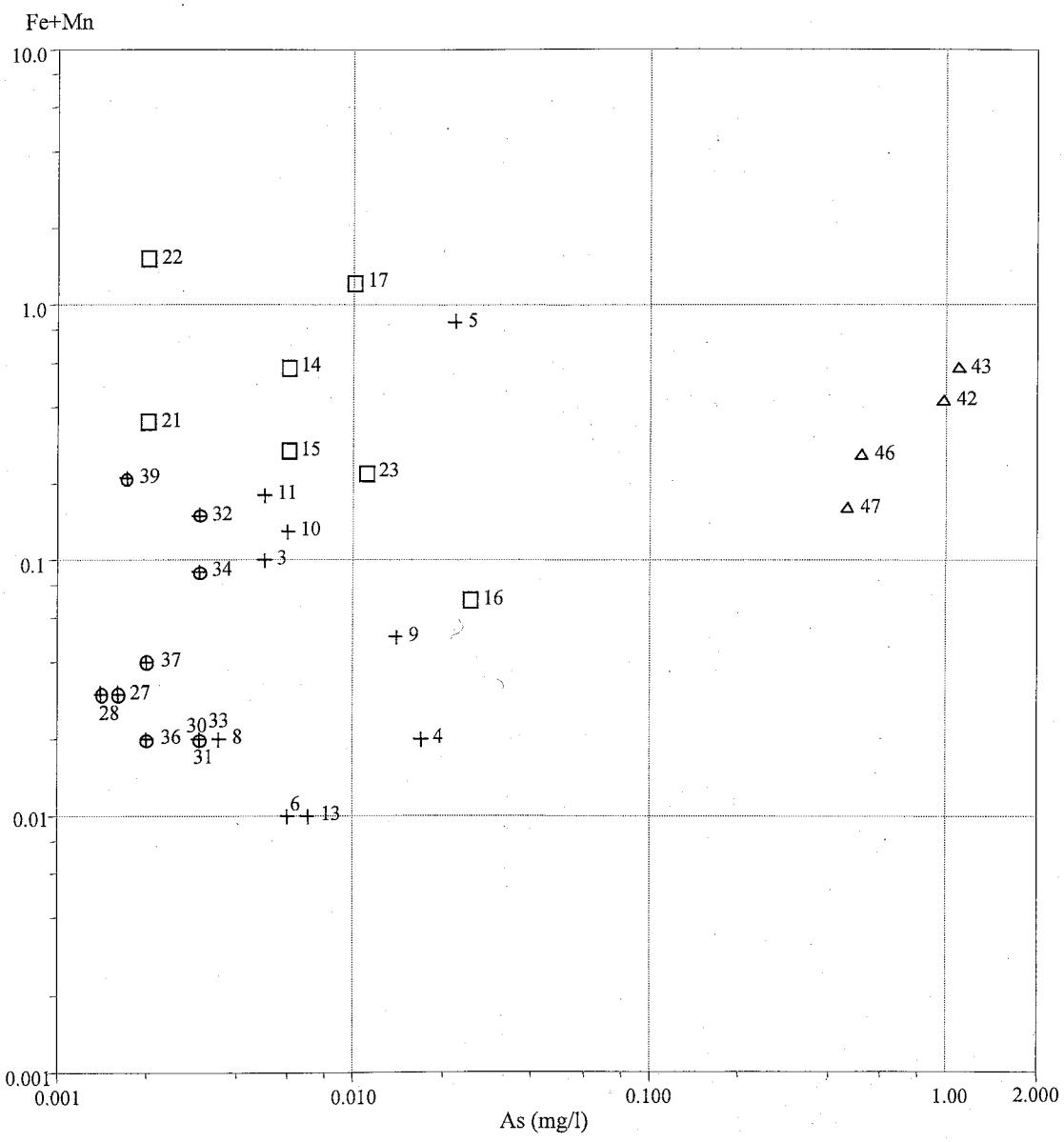


Figure 4.17. Log Arsenic vs. Iron and Manganese for all Field Samples.

iron and manganese correlation (r=0.6307). Samples from the Socorro (Nos. 1-13) and Truth or Consequences (Nos. 25-36) regions show no statistical covariation, with r values of 0.088 and 0.0332, respectively.

There are covariate trends shown when Cl/SO_4 is plotted against Na/K (Fig. 4.18). Truth or Consequences samples cluster and have a high Cl/SO_4 ratio. The Jemez Mountains samples cluster and have the greatest Cl/SO_4 ratio. The Bosque del Apache samples have the highest SO_4 concentrations and the greatest ratio of Na/K.

Results from the Jemez Mountains geothermal field

All samples in the Jemez Mountains contain high amounts of arsenic. The two springs at Spence Springs (Nos. 44, 45) have temperatures of 36°C (upper spring) and 41°C (lower spring). The arsenic concentrations at the two springs at Spence contain significantly lower levels compared to the other Jemez Mountains region samples, with concentrations ranging from 33 µg/l to 38 µg/l compared to 980 µg/l, 1100 µg/l, 520 µg/l, and 467 µg/l at Grotto Spring, Soda Dam Main spring, Travertine Mound, and the Gazebo, respectively. The arsenic at both Spence springs is dominated by As(V), with As(III)/As(V) ratios of 0.05 and 0.06. Arsenic at all other springs is predominantly As(III), with As(III)/As(V) ratios from 1.625, 18.33, 7.3, and 1.26, representing As(III) percentages of 62, 95, 88, and 56% for Grotto Spring, Soda Dam Main spring, Travertine Mound, and the Gazebo. The recovery of ASK2 aliquots is calculated by multiplying the concentration of the samples by two, to reflect the species concentration in the sample, and adding those concentrations together. Then, that result is divided by the arsenic concentration measured in the total arsenic sample and converted to a percentage. The

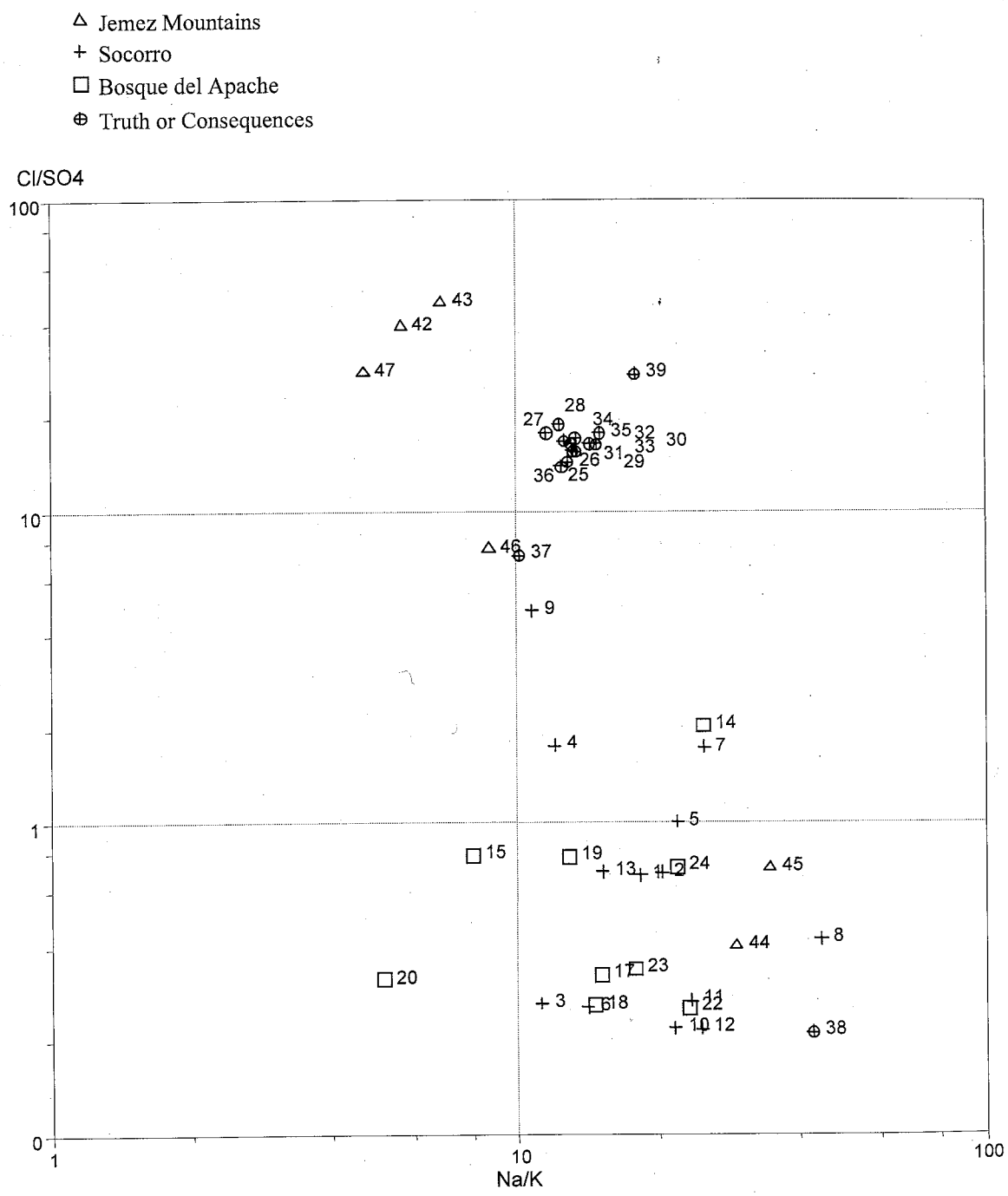


Figure 4.18. Log Chloride/Sulfate vs. Sodium/Potassium for all Field Samples.

recoveries are 90%, 84%, 97%, 95%, 83%, and 107% for Grotto Spring, Soda Dam (main spring), Spence Upper, Spence Lower, Travertine Mound, and the Gazebo, respectively. Recoveries of arsenic species average 92.6% with a standard deviation of 8.7%. A piper diagram is shown in Fig. 4.19, where it can be seen that there are two sample clusters, one for the two Spence springs, and one for the Jemez Springs and Soda Dam samples. The springs with high arsenic also contain high amounts of chloride. The higher temperature springs in the town of Jemez Springs had the greater amount of arsenic. There is a positive relationship between temperature and arsenic content of water at both Soda Dam or Grotto Spring, where arsenic values are high, 1100 and 980 μg/l, and temperatures are 46°C and 33°C, respectively. The Eh values are out of detection range for Soda Dam and both springs in Jemez Springs.

Results from the Socorro geothermal field

Arsenic concentrations in the Socorro geothermal system are low to elevated, with Socorro, Sedillo, and Cook Springs containing the highest amounts of arsenic, 35, 36, and 24 μg/l, respectively. Recoveries of arsenic species in the Socorro region average 102% with a 36% standard deviation. Major ion chemistry for all samples is illustrated in a piper diagram (Fig. 4.20), indicating that the thermal wells are sodium- and bicarbonate-rich and cluster while all other samples are dispersed. Samples that are elevated in arsenic are the Intor Company, School of Mines, and Industrial wells. The average pH is 7.89 ± 0.44, which is significantly higher than the samples in the Jemez Mountains area, which average 6.35 ± 0.70. Arsenic in the Socorro geothermal system is exclusively As(V); recoveries using the speciation kits range from 67% to 100%.

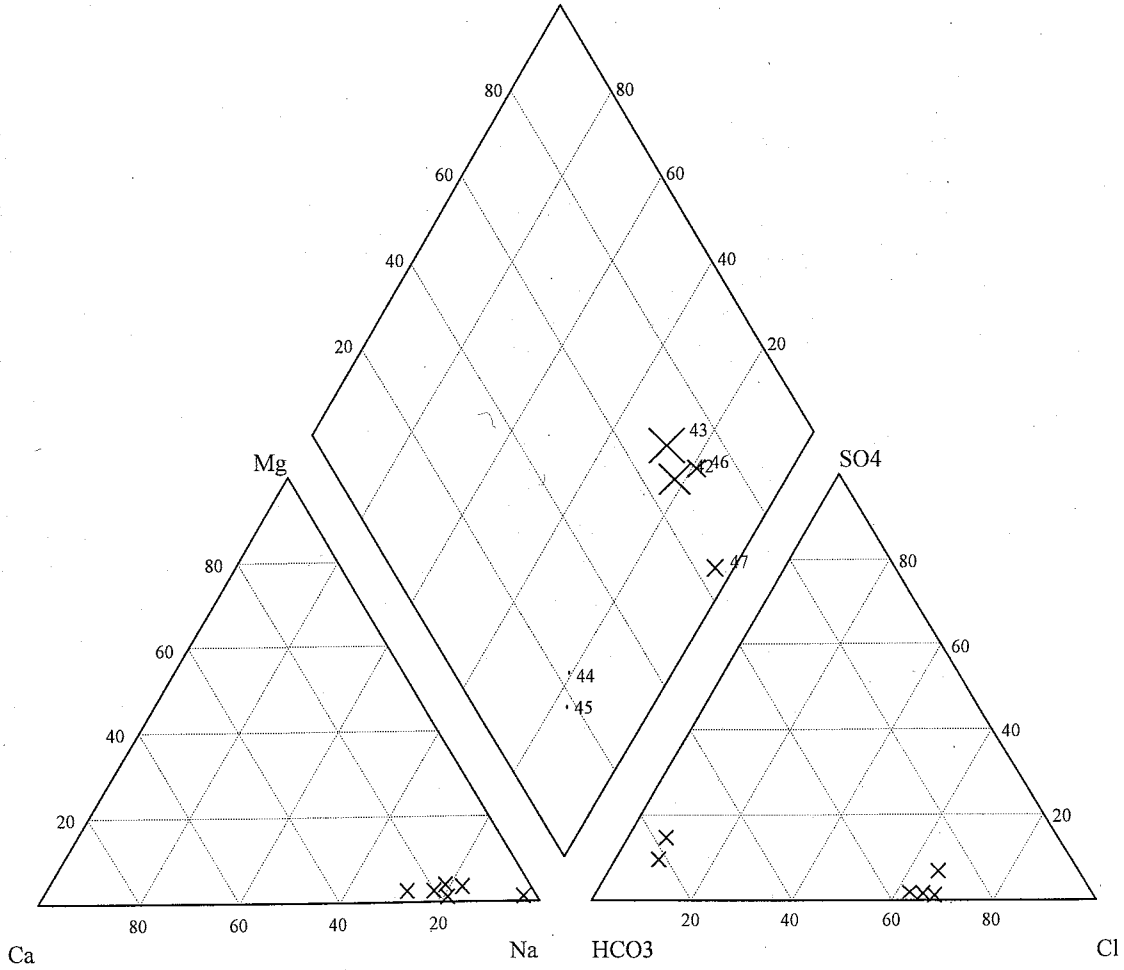


Figure 4.19. Piper Diagram of the Jemez Mountains Samples; Symbol Size Proportional to Arsenic Concentration.

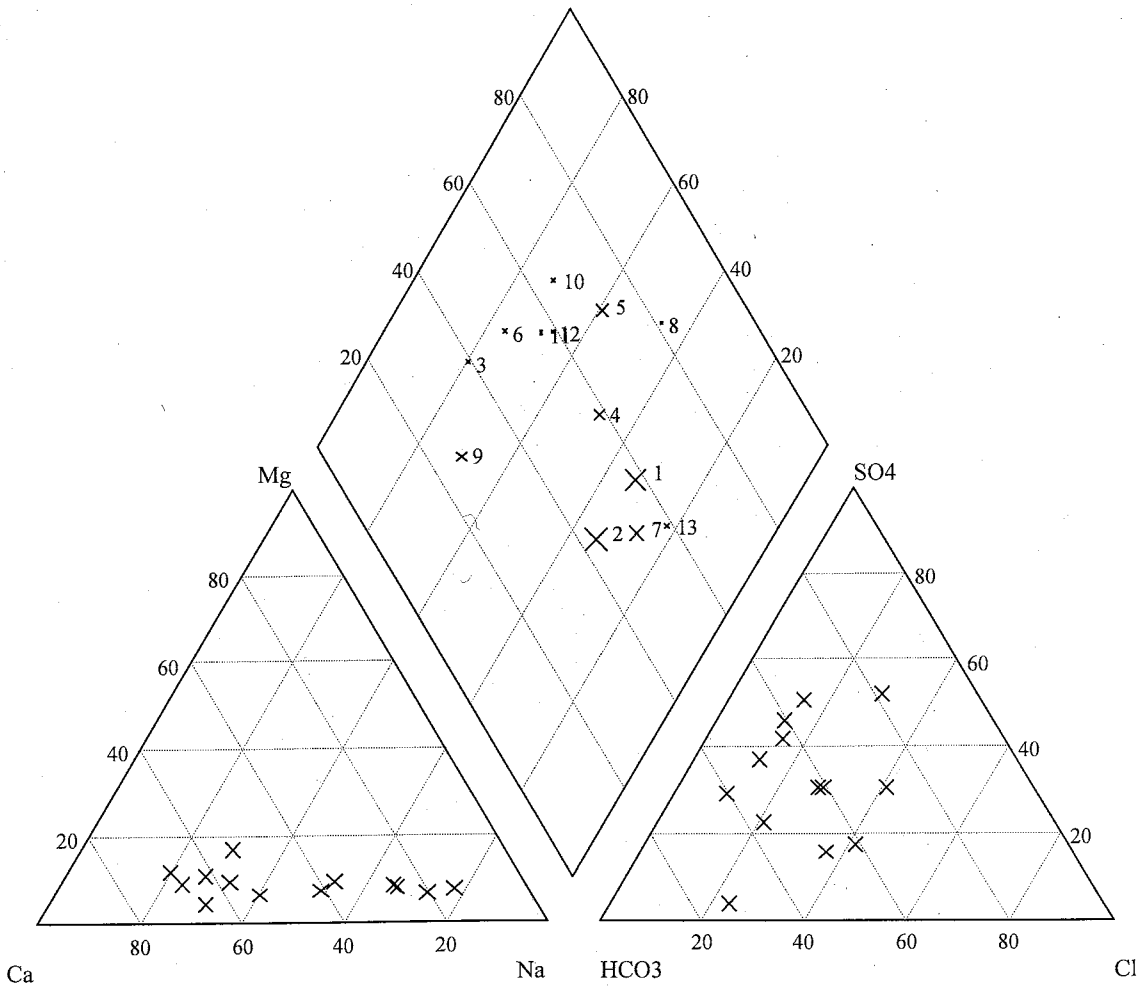


Figure 4.20. Piper diagram of the Socorro Field Samples; Symbol Size Proportional to Arsenic Concentration.

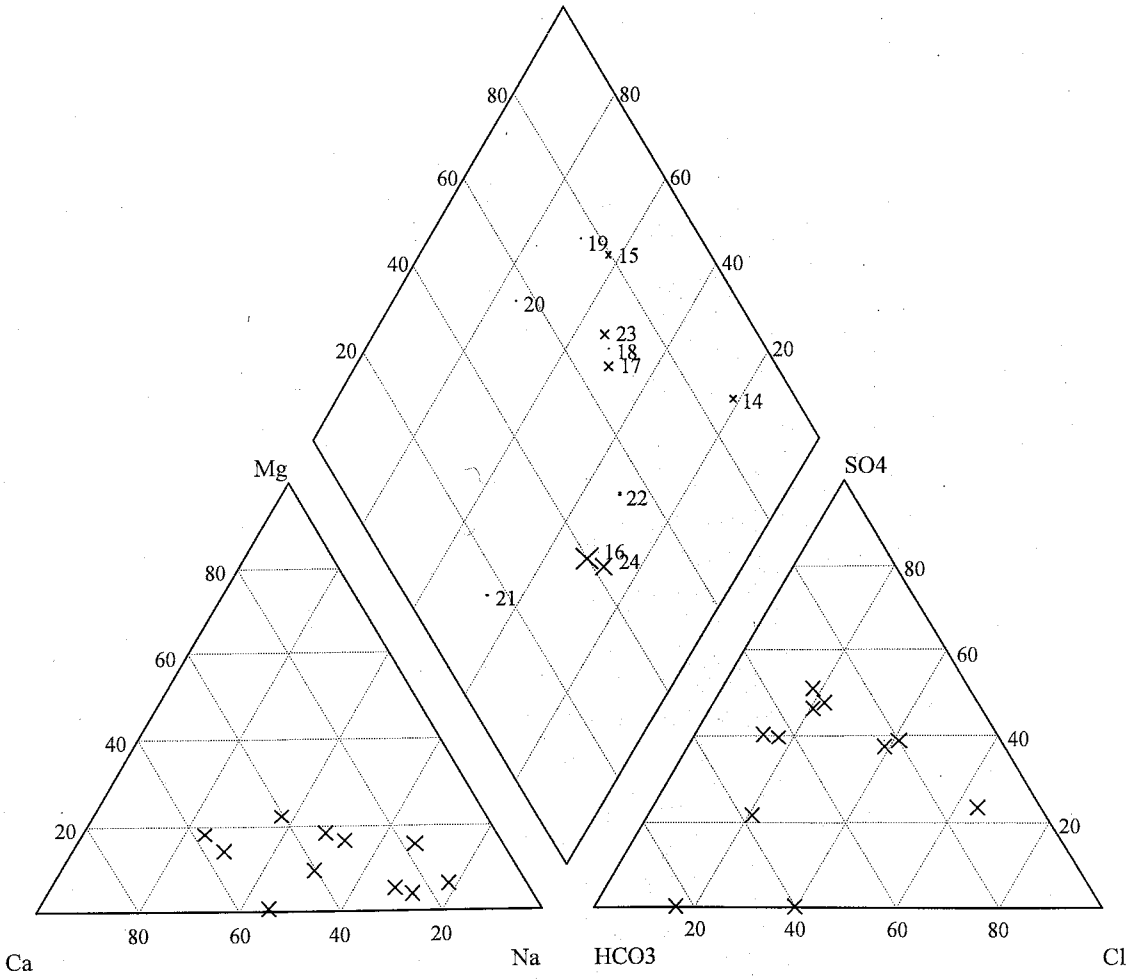


Figure 4.21. Piper Diagram of the Bosque del Apache National Wildlife Refuge Field Samples; Symbol Size Proportional to Arsenic Concentration.

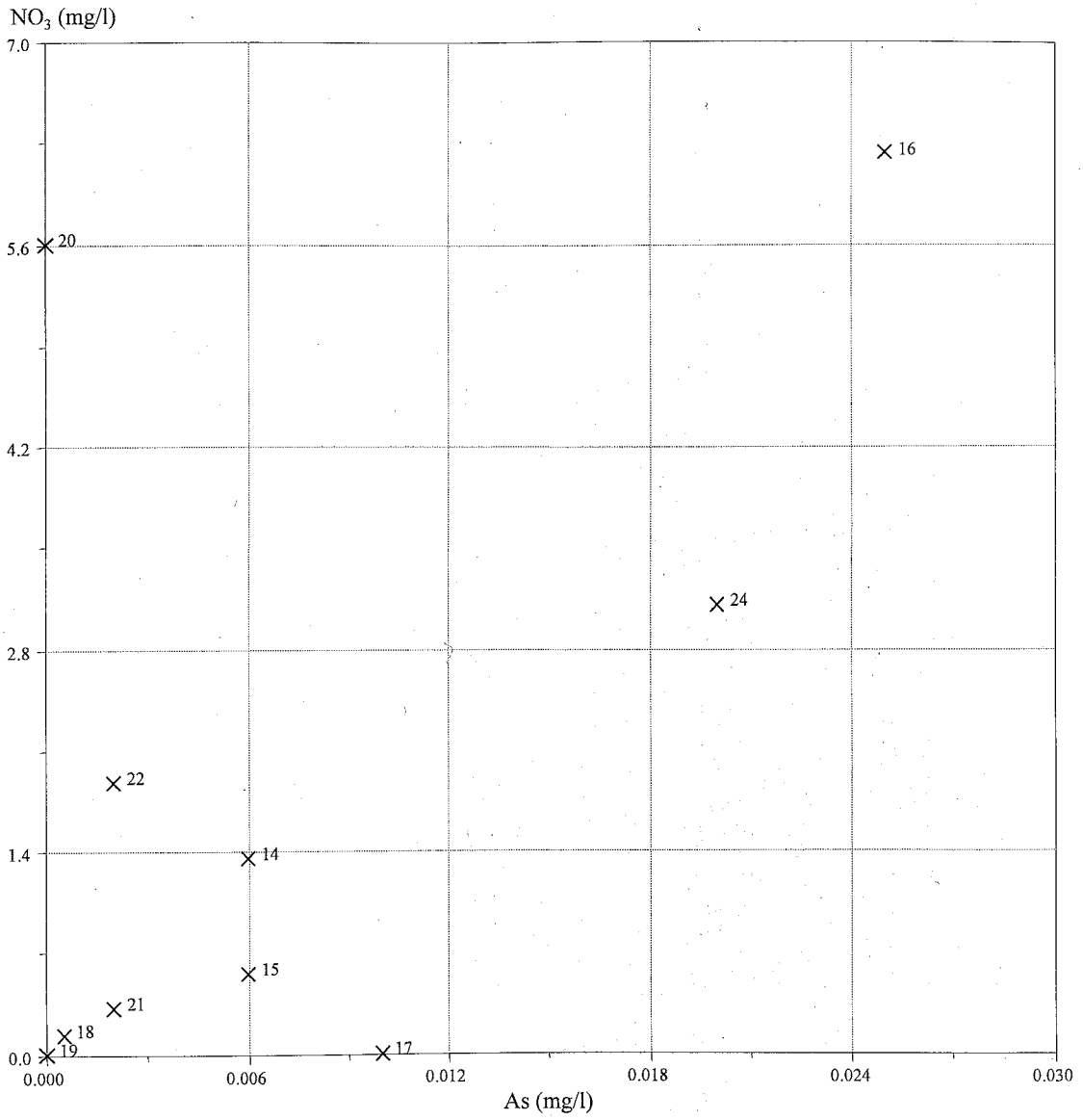


Figure 4.22. Arsenic vs. Nitrate for Bosque del Apache National Wildlife Refuge Field Samples.

Results from the Bosque del Apache

Arsenic concentrations range from low to elevated in the Bosque del Apache. The elevated samples spatially trend NNE. Arsenic is highest in the Headquarters, drinking water well, and irrigation well 3A, measuring 25, 20, and 11 µg/l, respectively. Arsenic species are 75% As(III), recoveries are 96% and 73% at both the Headquarters and drinking water well. No speciation data is available for the irrigation well 3A. The thermal well, with the highest TDS, contains arsenic 6 µg/l and has 86% As(III) with a 233% recovery. The thermal well contains the highest amount of chloride. This well is sampled twice (March 13, 2000, July 24, 2000), samples are analyzed several times showing little variation in water chemistry.

A piper diagram for Bosque samples is shown in Fig. 4.21. Like the waters in the Socorro district, it is high bicarbonate, high sodium waters that are highest in arsenic. Nitrogen levels range from below the detection level to a high of 6.23. When arsenic is compared to nitrate content of samples in the Bosque (Fig. 4.22), there is a positive correlation.

Results from the Truth or Consequences Region

In the Truth or Consequences region, 16 sites are sampled and all contained low concentrations of arsenic. Of the samples taken east of Elephant Butte Lake, the Hard Luck Crossing (No. 39) and Antelope wells (No. 40) are open metal shafts approximately 4 inches in diameter that required lowering a sample bottle down in order to get water. Analyses for Antelope well (No. 40) include Fe, Pb, and SiO_2. The Deep Well (No. 38) is a small outside guest house well; Hackberry well (No. 41) is used for watering range

cattle and the samples are taken from the tank, as the inflow is below the water line. These four samples are anomalous in location, temperatures for Deep Well and Hackberry well are 25.9 and 25.5°C. Los Animas Spring (No. 37) is a warm spring (28.5°C) located near Hillsboro, to the southwest of Truth or Consequences.

All of the springs and wells in the city of Truth or Consequences (Nos. 25-36) have temperatures near 42°C. Major ion analysis is shown in a piper diagram (Fig. 4.23). Samples from Truth or Consequences are extremely chloride and sodium rich and have calculated TDS that average 2556 mg/l.

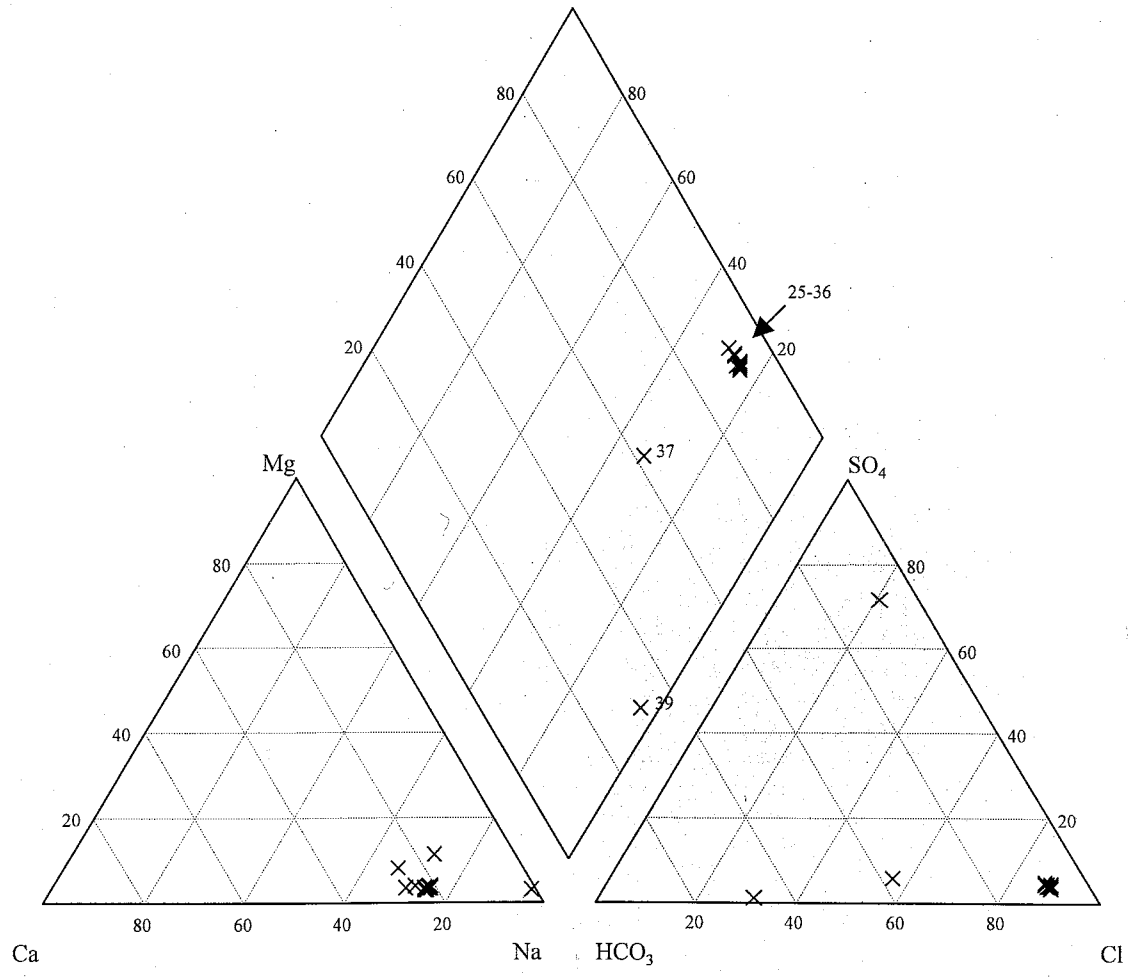


Figure 4.23. Piper Diagram of the Truth or Consequences Field Samples; Symbol Size Proportional to Arsenic Concentration.

Table 4.3. Arsenic Speciation and Temperature Results for all Field Sampling Locations.

Site	Sample ID	Total As	As(III)	As(V)	% Recovery	% As(III)	Temp °C
1	Socorro	0.035	0.000	0.030	85.7	0.0	30.4
2	Sedillo	0.036	0.000	0.024	66.7	0.0	33.1
3	Eagle Picher	0.005	0.000	0.004	80.0	0.0	21.2
4	Industrial	0.017	0.000	0.014	82.4	0.0	21.7
5	SoM	0.022	0.000	0.020	90.9	0.0	20.0
6	Olson	0.006	0.000	0.004	66.7	0.0	18.3
7	Cook Spring	0.024	0.000	0.024	100.0	0.0	24.4
8	Austin	0.004					18.0
9	Intor	0.014					22.2
10	Bushman	0.006	0.000	0.008	133.3	0.0	19.3
11	Holmes	0.005	0.002	0.006	160.0	25.0	18.7
12	Lattman	0.002	0.000	0.004	173.9	0.0	20.9
13	Hefner Lake	0.007	0.004	0.002	85.7	66.7	30.8
14	50BOS	0.006	0.012	0.002	233.3	85.7	32.0
15	17ABOS	0.006	0.006	0.000	100.0	100.0	21.1
16	BOSHQ	0.025	0.018	0.006	96.0	75.0	21.7
17	12ABOS	0.010	0.008	0.004	120.0	66.7	19.1
18	13BBOS	0.001	0.000	0.000	0.0	0.0	19.0
19	1NEBOS	0.000	0.000	0.000	0.0	0.0	19.4
20	9NWBOS	0.000	0.000	0.000	0.0	0.0	19.8
21	9NEBOS	0.002	0.000	0.000	0.0	0.0	17.0
22	1NWBOS	0.002	0.000	0.000	0.0	0.0	17.7
23	3NBOS	0.011	0.006	0.002	72.7	75.0	19.0
24	BOSDW	0.020					26.6
25	Riverbend	0.002	0.000	0.000	0.0	0.0	43.0
26	Indian Springs	0.001	0.000	0.000	0.0	0.0	40.5
27	Geronimo Springs	0.002	0.000	0.000	0.0	0.0	42.3
28	Charles Motel	0.001	0.000	0.000	0.0	0.0	43.6
29	Marshall #4	0.004	0.000	0.000	0.0	0.0	44.0
30	Marshall #5	0.003	0.000	0.000	0.0	0.0	42.0
31	Marshall #2	0.003	0.000	0.000	0.0	0.0	44.3
32	Marshall #3	0.003	0.000	0.000	0.0	0.0	43.8
33	Marshall #1	0.003	0.000	0.000	0.0	0.0	43.1
34	Marshall DW	0.003	0.000	0.000	0.0	0.0	43.3
35	Artesian		0.000	0.000	0.0	0.0	43.1
36	Hay-Oh-Kay	0.002	0.000	0.000	0.0	0.0	42.1
37	Los Animas	0.002	0.000	0.000	0.0	0.0	28.5
38	Deep Well	0.000	0.000	0.000	0.0	0.0	25.9
39	Hard Luck Crossing	0.002					
40	Antelope Well						25.5
41	Hackberry						33.0
42	Grotto Spring	0.980	0.546	0.336	90.0	61.9	46.3
43	Soda Dam main	1.100	0.880	0.048	84.4	94.8	36.1
44	Spence Upper	0.033	0.002	0.030	97.0	6.3	41.9
45	Spence Lower	0.038	0.002	0.034	94.7	5.6	71.4
46	Travertine Mound	0.520	0.380	0.052	83.1	88.0	71.0
47	Gazebo	0.467	0.278	0.220	106.6	55.8	

For the most part, samples with higher arsenic concentrations tended to have better recoveries. Samples that have poor recovery tend to be samples that have low

arsenic concentrations. For example, the Bosque del Apache Thermal well (No. 14) sample has a total arsenic value of 6 μg/l, while the species have arsenic concentrations of 2 and 12 μg/l. This means that the GFAA species results are 1 and 6 μg/l, because the values are re-calculated to reflect the concentration of the species before dilution through the column. A 233% recovery is calculated for this example. Although this recovery is very poor, it is not surprising. Laboratory standards tests showed that recoveries tended to be highest approaching the detection limit. The eight samples that had recoveries lower than 80% or greater than 120% are all from samples with arsenic totals of 10 μg/l or less, with the exception of Sedillo Springs. Sedillo Springs has a total arsenic concentration of 36μg/l and a total species recovery of 66.7%. When all field samples are analyzed, the mean recovery is 104.7% and median recovery is 92.8%. Considering the external reference standards had an error of ±11.4%, the field samples have good recoveries.

DISCUSSION

ASK2 Speciation Method

Limitations of the Method

Total arsenic concentrations of less than or equal to 10 μg/l are not separated well using this method. This is indicated in all tests of the kit. Laboratory samples taken in 2-ml aliquots and two single aliquots both show that recoveries increase as quantification approaches the detection limit. Field tests also showed that water samples with arsenic concentrations above 10 μg/l had recoveries closer to 100%, while samples with arsenic concentrations tend to have spuriously higher recoveries.

The limitation of the kit to waters with low arsenic concentrations is not a concern. Only municipalities with elevated arsenic concentrations will face arsenic remediation. Municipalities are expected to be the biggest users of this kit. Therefore, the target application of this kit is for waters with elevated arsenic concentrations.

Functional Parameters

The eluent volumes required to separate As(III) from As(V) are very specific to the degree of resin conversion. In our research, we found that the same conversion procedure resulted in slightly different elution behavior for As(V). The eluent volume required to elute As(V) from resin that had been converted twice is one and a half times

greater than resin that had undergone a single conversion. The species are separated more with greater conversion of the resin to the acetate form.

It has been shown that DMA and MMA will coelute with As(III). If one of these organic species is present in the sample, As(III) will be indicated. This can become a concern in surface waters. The user should keep in mind that As(III) will statistically be overestimated, while As(V) will statistically be underestimated.

Recovery Calculations

Recoveries are calculated for all experiments by multiplying the volume of eluent by the concentration in the eluent and dividing by the known input concentration to get a percentage. In Tables 4.1 and 4.2, the mean and standard deviation of these recoveries are shown for ASK2 columns. The As(III) species is consistently overestimated (>100%), while As(V) is significantly lower at the same concentrations. One reason for this could be that the GFAA uses an As(V) standard, and the overestimation of As(III) may simply be an artifact of the standardization and detection methods. In the ASK4 columns, one of the pervasive problems with the operation of the kit is the incomplete stripping of As(V) from the column, which allows As(V) to elute in the DMA range. This retention of As(V) may also be occurring in ASK2 columns, accounting for the decreased recovery of As(V).

The recoveries in these experiments are calculated from the concentrations of individual species. Other researchers (e.g. Wilkie and Hering, 1998; Clifford and Ghurye, 2000) calculate As(V) by difference. In their calculations, As(III) is eluted from an anion exchange resin and analyzed. A separate total arsenic replicate sample is analyzed. The

total sample minus any As(III) detected is reported as As(V). No As(V) is measured, but a value is reported. The fundamental assumption in this calculation method is that all arsenic will be recovered and that analytical and experimental error is minimal. It is shown that experimental error can be large. Calculating As(V) concentrations by difference has the potential to compound error that may not be apparent. Our method minimizes error by analyzing each species and comparing these values to a total arsenic replicate.

Sample volumes are doubled in the elution, so concentrations reported by the GFAA are half of the concentration of the species in the original water sample. Species aliquot concentrations are doubled in the results section. This is equivalent to showing the concentration of species in the water sample, rather than the eluent.

Operation of the Method

The method is highly successful within the limits and functional parameters stated above. The kit is able to separate arsenic species in the field and laboratory with minimal error. Ion interferences in field samples do not affect the speciation results. Water samples are taken from a variety of areas and represent very different water types and arsenic levels. In all cases, species had the best recovery when total arsenic concentrations are above 10 μg/l. The kit is easy to use in the field.

ASK4 Speciation Method

Limitations of the Method

There is considerable investigation into solving the late arsenic peak. Analyses of blanks show that there are peaks of about 2 μg/l in regions that should have no arsenic in them. These peaks correlate to the late As(V) peaks. Although the peaks are very near the detection limit of the GFAA, they are consistently present in all runs. The peaks are thus detections of arsenic in the samples. In the blank analyses, arsenic is most likely present due to concentration and elution of sub part per billion levels in the eluent or regeneration procedure.

Suggestions for further work that utilize a modification of the Grabinski method include increasing the sample volume to greater than 2 ml. With a sample volume of 2 ml and an eluent volume of 120 to 200 ml, the sample dilution is close to 100-fold. Other focuses might include investigating other eluents that might strip the resin of arsenic better (e.g. hydrochloric acid), shortening the cation resin length to decrease the likelihood that As(V) may remain trapped on the resin, or investigating the removal of the lower (anion) column after elution of As(III), MMA, and As(V) and eluting DMA from the anion column rather than going through the cumbersome process or desorbing DMA from the cation resin only to sorb it to the anion resin. Work done subsequent to the completion of this study is not included.

Functional Parameters

The quantity of As(V) is greatest when larger aliquots (30 ml rather than 8 ml) of acid (0.2 M TCA) are used. Enough arsenic is retained in the resin or concentrated from the eluent that all runs have peaks in the DMA range. However, there is good separation of As(III), As(V), MMA, and DMA at high arsenic concentrations.

Arsenic Speciation and Abundance in Thermal Areas

Field Testing of the ASK2 Kit

Natural water samples were collected from 47 field sites, and the ASK2 speciation kit was used to analyze 38 of these samples. Water quality ranged from drinking water to high chloride waters (Jemez Mountains samples), to high TDS waters (Truth or Consequences samples). The arsenic recovery varies between 66.7% and 233%, with an average of 104.7%. Although the average is good, this is the result of high and low recoveries from samples with total arsenic concentrations lower than 10 μg/l. When samples containing >10μg/l are analyzed, the recoveries are between 66.7% and 120.0%, with an average of 90.7%, which is very good. The field kit works better on field samples than RO water.

Jemez Mountains Geothermal Field

The Jemez Mountains geothermal system has deeply circulating groundwaters that have been strongly altered (Rao, 1996). These waters have been diluted with near-surface recharge water. Mixing of deep thermal water with shallow recharge water is a likely explanation for the positive trends seen between the high arsenic and elevated

arsenic samples. Arsenic correlates positively with chloride, total dissolved solids, and with combined iron and manganese. Silica, As(III) percentage, and temperature show a positive trend, increasing with arsenic concentration. Thus, the water samples from the Jemez Mountains geothermal area have many characteristics of thermal waters as described by Ballantyne and Moore (1988).

The removal of arsenic from groundwater may be due to surficial oxidation and coprecipitation with Fe and Mn, as observed by Wilkie and Hering (1998) and Sriwana et al. (1998). An alternate explanation for the decrease in arsenic concentration may be due to dilution of the water rather than removal of arsenic. In the Jemez Mountains, dilution is a more likely explanation because elevated and high arsenic samples show positive correlations with most measured parameters (Cl^-, TDS, Na^+, K^+, HCO_3^-). It is also apparent that the dilution waters have the capacity to oxidize As(III) to As(V) because both elevated arsenic samples are dominated by As(V), while high arsenic samples contain predominantly As(III).

Socorro Geothermal Area

Arsenic is found in elevated levels in the thermal springs in Socorro. Arsenic is also found in other municipal wells (Industrial, School of Mines) that are deep and pump relatively large volumes of water. There are several possible sources of arsenic in rock that could be contributing to elevated levels of arsenic in the thermal springs. First, waters recharging from the Magdalena Mountains is heated by the geothermal gradient and the higher temperatures allow arsenic to be leached from rhyolites near the springs.

An alternate explanation is that rocks in the Socorro Peak area have undergone significant hydrothermal alteration and mineralization, thus being enriched in arsenic. The most significant evidence that arsenic could be leaching from ancient mineralized systems is the presence of the mineral mimetite, which is arsenic bearing. The ancient hydrothermal system that deposited metals in Socorro Peak is possibly related to the Luis Lopez Manganese District (Lasky, 1932). Thermal springs show a negative correlation of arsenic vs. TDS, which is not observed for the entire Socorro sampleset. Shallow, low TDS waters could be scavenging sorbed arsenic from the fractured rhyolite or hydrothermally altered rock. Slightly higher temperatures are likely assisting the dissolution of arsenic from pore spaces. The arsenic-bearing springs coincide spatially with deep, Rio Grande Rift faults. The faults are able to provide a conduit for fluids to discharge to the surface, thus, all three springs are located on the fault line (Gross and Wilcox, 1983; Mailloux et al., 1999).

The suggestion from the literature that thermal waters contain higher concentrations of arsenic than nonthermal waters (e.g. Onishi and Sandell, 1955; Onishi, 1969) is somewhat true for Socorro samples. All three thermal springs contain elevated arsenic. The springs in Socorro do not have a "truly thermal characteristic," as is noted by Gross (1983), so it is not surprising that all arsenic in Socorro is As(V). If the mobilization mechanism is the reduction of As(V) to As(III), then Eh conditions are not favorable for maintaining the As(III) species, and arsenic is oxidized to As(V). It is more likely that arsenic is dissolved into the warmer waters that discharge in the three thermal springs. All three springs have very similar water chemistries. Temperatures, arsenic concentration, bicarbonate, and Na/K ratios all decrease from Sedillo, to Socorro, to

Cook Spring, while pH and conductivity increase. All other measured parameters are very close to one another.

Hefner lake has an arsenic concentration of 7 µg/l, which suggests that arsenic is present at or above that concentration naturally in Socorro groundwater. Arsenic in the lake is probably an underestimation of aquifer arsenic because clays found in the lake would likely sorb As(V), lowering the concentration in the lake relative to the source water.

A correlation to well production volume is found, which is similar to the findings of Kelly et al. (1996). Wells across Socorro that are low volume producers (e.g. Dr. Austin's well, NM Tech wells) have low levels of arsenic, while large producers (e.g. School of Mines Well, Intor well) have elevated arsenic concentrations.

Bosque del Apache

Only two wells in the Bosque del Apache have arsenic levels greater than 10 µg/l, the Headquarters and Drinking water wells. Speciation samples are not collected on the drinking water well. All other samples in this study area have arsenic concentrations lower than 10 µg/l.

This study shows that the thermal well does not contain the levels of arsenic expected from Branvold's study (2001). During the time samples are taken for the Branvold study, the thermal well was being used routinely (Branvold, personal communication). During this study, the well had not been pumped in many months. It is possible that increased pumping led to higher arsenic concentrations in the previous study. It is noted by Kelly and Reinert (1996) that increased pumping in the Santa Fe

Formation led to increased levels of arsenic in the drinking water, and it is possible that this "pumping phenomena" is responsible for the increased arsenic with drawdown. It is unlikely that the thermal well is contaminated anthropogenically.

The wells with the greatest concentrations of arsenic are the Headquarters and Drinking water wells. One explanation for the levels of arsenic suggests that anthropogenic input of arsenic in the environment from farming activity is responsible for the elevated levels of arsenic seen at these two locations. Samples with arsenic concentrations >10 μg/l correlate with nitrogen. It is possible that an arsenic-reducing bacteria is reducing arsenic in these irrigation wells. The increased nutrient load, farmland, and animal waste provides an environment for increased microbial and bacteriological activity. Another explanation suggests that organic arsenic present. If organic arsenic is present, then it would coelute with As(III). Arsenic is dominated by As(III), which could be MMA or DMA, indicating that pesticide usage may be responsible for the increased arsenic concentrations near the Headquarters building.

Truth or Consequences Geothermal Area

The Truth or Consequences geothermal waters have low arsenic concentrations. Thermal waters had not been extensively analyzed, despite numerous public bathhouses and uncounted private baths that take advantage of the shallow thermal (~ 40°C) waters. Reports from bathhouse brochures of arsenic levels at 50 μg/l cannot be substantiated. Arsenic in previous studies (e.g. Indian Springs, 2000) is likely at the instrumental detection limit, and is probably reported as such. However, bathhouse brochures purport that levels of arsenic are at 50 μg/l, and therefore the ASK2 kits were used.

Unfortunately, the arsenic species cannot be quantified because concentrations of the aliquots are below detection.

Truth or Consequences waters have very high TDS, which exceeds 2.5 g/l. Arsenic levels are the lowest of all thermal areas that are investigated in this study. The greatest difference comparing this area to other thermal systems analyzed in this study, is that this region does not have silicic volcanic rock. The aquifer is in fossiliferous Pennsylvanian limestones. The nearest volcanic rocks are precambrian granites that underlie the sedimentary package.

Arsenic Abundance and Speciation

There are two distinct types of systems that have been investigated in this study. The first system is represented by the Jemez Mountains system. The waters are circulating in an extremely high temperature volcanic geothermal system. This system is comparable to Yellowstone (Thompson, 1979). While Thompson (1979) did not measure As(III) concentrations in Yellowstone waters, he concludes that As(III) is dominant and is oxidizing and coprecipitating with iron and manganese. In the Jemez Mountains region, total arsenic and iron and manganese correlate positively, indicating that this mechanism of arsenic removal is possible. Another explanation for the for the decrease in arsenic concentration in locally diluted springs, is dilution. There appears to be mixing and dilution of strongly altered, hot, chloride waters with shallow, low TDS waters. In the process of dilution, As(III) is being oxidized to As(V). Rapid oxidation of As(III) to As(V) is observed by Wilkie and Hering (1998), who speciated arsenic in an Eastern Sierra Nevada geothermal system. Overall, high temperature geothermal systems in

volcanic regions tend to have the highest concentrations of arsenic and are most likely to contain the highest proportions of As(III).

The second type of system that is represented here is a non-magmatic basin thermal system. Arsenic concentrations are controlled mainly by aquifer geology. Arsenic levels range from below detection to ~ 50 μg/l in these three areas. An increase in temperature is not a good indicator of increased arsenic in these thermal waters.

In the Socorro region, rhyolite that has been altered by an ancient, arsenic-bearing hydrothermal system appears to be the source of arsenic in groundwater. This system is most like the Bowena copper mine in British Columbia described by Boyle et al. (1998). In the region described by Boyle et al. (1998), deep faults in an arsenic-bearing copper porphyry provide a conduit for arsenic enriched fluids. The Socorro region has elevated arsenic concentrations in fault-controlled springs at the base of Socorro Peak. Another interesting phenomenon is noticed in the Socorro region. It appears that wells that have the greatest discharge and are deepest have elevated arsenic, while low discharge wells have low arsenic concentrations. Kelly and Reinert (1996) noted that arsenic concentrations increased as pumping volume and duration increased in the Santa Fe Formation, Bernalillo, New Mexico. In the Bosque del Apache, sand and gravel with some clay layers form the aquifer. It is not clear whether the elevated arsenic levels found at this location are naturally occurring, or if the aquifer is not arsenic bearing. The wells with elevated arsenic are proximal to the Headquarters building, and it is possible that anthropogenic arsenic is locally contaminating the water. Arsenic concentrations are low to elevated and show a negative trend with TDS. In the Truth or Consequences area, the samples have low to nondetectable concentrations of arsenic. These two regions are

examples of thermal systems that contain low to elevated concentrations of arsenic. Thermal areas are typically thought to have high levels of arsenic, but Onishi (1969) recognized that arsenic concentrations in some thermal systems are as low as 2 μg/l. This study emphasizes the need to understand the geologic setting of thermal systems in order to predict the abundance and speciation of arsenic in thermal waters.

CONCLUSIONS

1. The ASK2 kit works well to separate As(III) from As(V) in waters that have total arsenic concentrations >10 μg/l. The separation yields high recoveries and quantifies both species.

2. The ASK2 kit does not separate As(III) from As(V) well in waters with total arsenic concentration <10 μg/l.

3. A problem with the ASK2 kit is that MMA and DMA coelute with As(III).

4. In the ASK4 method, As(V) is retained in the resin, eluting as a "false DMA peak" at all concentrations.

5. The ASK4 method needs further work. Suggestions include increasing the sample volume, decreasing the anion resin volume, and testing at concentrations that are politically relevant (i.e. >10 μg/l, <50 μg/l).

6. Arsenic concentrations are highest in the volcanic aquifer that have subsurface temperatures greater than 250°C. In this system, meteoric water is highly altered by magmatic interaction. The arsenic in this system is dominated by As(III). Waters that are further diluted by near-surface recharge (Spence springs) have proportionally less arsenic, and the arsenic is As(V).

7. Arsenic concentrations in basin thermal waters range from low to elevated, and all arsenic is As(V). There is an inverse relationship to arsenic and TDS in these waters. No other parameters show distinct correlations with arsenic.

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