United States Air Force Research Laboratory

Analysis of Trace Level Perchlorate in Drinking Water and Ground Water by Electrospray Mass Spectrometry

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Biosciences and Protection Branch
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FOR THE DIRECTOR

//SIGNED//

MARK M. HOFFMAN
Deputy Chief, Biosciences and Protection Division
Air Force Research Laboratory
**Analysis of Trace Level Perchlorate in Drinking Water and Ground Water by Electro spray Mass Spectrometry**

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**Abstract:**
A new method involving the use of electro spray mass spectrometry was developed for the detection of trace levels of perchlorate in ground water and drinking water. Electro spray mass spectrometry was shown to be both sensitive and selective for the detection of perchlorate in aqueous matrices. The method detection limit was calculated to be 0.38 ppb. Improvement of more than order of magnitude over the currently accepted method. Percent recovery for the detection of perchlorate with this method was found to be 82.4%.
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PREFACE

This report summarizes the research that began in May 1998 and was completed in September 1998, under Department of the Air Force Contract No. F41624-96-C-9010. The study, as described in this report, was conducted under the collaboration among the State of Utah, Department of Health, and Department of Environmental Quality, and the Department of the Air Force. Major Steve Channel served as Contract Technical Monitor for the United States Air Force, AFRL/HEST.
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LIST OF ABBREVIATIONS

ac       alternating current
amu      atomic mass units
API      atmospheric pressure ionization
ES-MS    electrospray mass spectrometry
CE       capillary electrophoresis
cm       centimeter
dc       direct current
HPLC     high performance liquid chromatography
IC       ion chromatography
i.d.     inner diameter
ISE      ion selective electrode
kV       kilovolt
L        liter
MDL      method detection limit
μl       microliter
mm       millimeter
mmol     millimole
ppb      parts per billion
ppm      parts per million
psi      pounds per square inch (pressure)
RL       reporting limit
stdev    standard deviation of the values
S/N      signal to noise ratio
t        student t factor
TDS      total dissolved solid
UV       ultra violet
V        volt
ANALYSIS OF TRACE LEVEL PERCHLORATE IN DRINKING WATER AND GROUND WATER BY ELECTROSPRAY MASS SPECTROMETRY

SECTION 1: INTRODUCTION

The recent discovery of perchlorate contamination in the ground water of several western states has caused concern for the quality of the drinking water supply. The current accepted level for the presence of perchlorate in drinking water is 18 parts per billion (ppb), but has been found at concentrations as high as 37 parts per thousand in ground water near munitions manufacturing and testing facilities.1-11 Ammonium perchlorate has been found in commercial fertilizers and is used as the oxidizer and main ingredient in solid rocket propellants, fireworks, and munitions. Perchlorate contamination has also been found in areas such as Texas, where fertilizers are widely used to maintain land for cattle farming. Two of the main ingredients in these commercial fertilizers, potash and Chilean nitrate, have been shown by Air Force Research Laboratories to contain up to 0.57 percent by weight perchlorate. Although these deposits contain the necessary ingredients for fertilizers, they are also a very rich source of perchlorate.9-11

Perchlorate is known to interfere with the uptake of iodide by the thyroid in order to produce necessary hormones. Many toxicological studies are currently taking place in which the reference dose for perchlorate in humans is being determined and the possibility of developmental toxicity and genotoxicity is being analyzed.8 The growing interest in the presence of perchlorate in ground water and drinking water has brought about a need for viable methods of detection that possess a high sensitivity and selectivity for perchlorate.
The perchlorate anion has a mass to charge ratio of 99.1 amu. As a result of the relatively large diameter and the small, highly delocalized charge of the perchlorate anion, it is only weakly basic toward most Lewis acids. Most perchlorate salts are therefore highly soluble in water. Although perchlorate forms weak salts, it is a polarizable anion. Perchlorate has a small hydrated radius and a low hydration energy, and thus, is able to form strong complexes with large, delocalized, organic cations.

Early techniques for perchlorate analysis, such as gravimetric analysis\textsuperscript{12-16} and liquid-liquid extraction/spectrophotometry\textsuperscript{17-22}, relied on the ability of perchlorate to form complexes with large organic dyes, such as brilliant green and methylene blue. However, these methods are not selective for the determination of perchlorate. Other anions commonly found in drinking water, such as phosphate, nitrate, and chlorate, can also complex with these dyes. Ion pair high performance liquid chromatography (HPLC)\textsuperscript{23-24}, capillary electrophoresis (CE)\textsuperscript{25-31}, and ion selective electrode (ISE)\textsuperscript{31-32} have also been used in perchlorate analysis. Yet these methods do not have the necessary sensitivity at trace ppb levels.

The current method of choice involves the use of ion chromatography coupled with a conductivity detector.\textsuperscript{33-37} This method has an accepted sensitivity of 4 parts per billion (ppb). However, there are some substances found in drinking water which may interfere with the chromatographic separation of perchlorate, and the conductivity detector is not selective for the determination of perchlorate.\textsuperscript{38,39} Additionally, questions have been raised as to the sensitivity and robustness of this technique. For example, it has been demonstrated, by Air Force Research Laboratory Operational Toxicology Branch (AFRL/HEST), that high levels of total dissolved solid (TDS) can completely block the signal of perchlorate in conductivity measurements. Therefore, it is necessary to develop a method for perchlorate analysis that would be selective for
perchlorate and would have a sensitivity equal to or greater than that of the current ion chromatography methods.

Coulometric electrochemical detection has been suggested as an alternative method for perchlorate analysis due to its increased sensitivity and the ability of the instrument to selectively detect anions that cannot be separated through chromatography. Despite the apparent advantage in the application of coulometry, it has been shown that due to instrument limitation on current detector technology, the reduction of perchlorate is not feasible.  

Electrospray mass spectrometry is an ideal option for perchlorate analysis due to the selectivity, sensitivity, and efficiency of the instrument. Through electrospray mass spectrometry, it is possible to selectively monitor the ion of choice. When the spectrometer is tuned to detect a specific mass to charge ratio, the other anions are filtered out in the quadrupoles. Consequently, the background signal is reduced, and sensitivity is enhanced. Since the instrument selectively monitors the species of interest, there is no need for chromatographic separation before injection into the mass spectrometer. As a result, the analysis time for prepared samples is reduced from 20 minutes to 30 seconds. Electrospray ionization is an ideal method for the ionization and vaporization of perchlorate, due to the ability of this technique to volatilize non-volatile substances, such as perchlorate.

Electrospray ionization is an atmospheric pressure ionization (API) technique. Within the API chamber, a voltage of 3-8 kV is applied to the electrospray probe. Consequently, the droplets are electrically charged as liquid sample is ejected from the probe. The positive ions are driven to the surface of the droplet, which disrupts the surface tension and disperses the drop into a fine spray of droplets. These droplets are then driven toward the heated capillary by the voltage gradient set between the capillary and the electrospray probe, and by the inert sheath gas,
which surrounds the probe and pushes the droplets forward. As the droplets approach the heated capillary, the increased temperature causes the volatile solvent to evaporate off. Eventually, the electrical charge within the droplets reaches the Rayleigh Stability Limit. This is the point where the intermolecular forces overcome the surface tension, and the droplet explodes again. This process is repeated until the analyte is either ejected into the gas phase by electrostatic forces, or until the solvent is completely stripped from the anion. The ions subsequently pass through the heated capillary and tube lens into an intermediate vacuum region, where they are focused by the ion optics.\textsuperscript{42-43} The perchlorate anions eventually pass into the quadrupole mass filters.

The quadrupole mass filter consists of four parallel rods that serve as electrodes. Two of the rods are connected to the positive end of a DC terminal, and two of the rods are connected to the negative end. Additionally, a transverse AC potential is also superimposed upon each pair of rods. When the spectrometer is in negative ion mode, the negative poles filter the lighter ions. In the negative poles, the AC current pulls the lighter anions into the poles, where they will be neutralized, while the DC potential helps to stabilize the trajectory of the heavier anions. In the positive poles, the first half of the AC cycle directs the lighter ions to the center of the channel. This offsets the movement of the negative anions toward the oppositely charged poles. Since the AC current does not as easily affect the heavier ions, they are drawn into the poles and neutralized. Hence, the positive poles filter the lighter anions, and the negative poles filter the heavier anions, and only ions within a very narrow range of mass to charge ratios are actually allowed to reach the detector.\textsuperscript{42,45-46}

The ability of the quadrupoles to selectively monitor the perchlorate anion and to filter out the interference anions commonly contained in water, and the ability of the electrospray ionization to volatilize non-volatile perchlorate for analysis by mass spectrometry allows for the
sensitive and selective determination of perchlorate. The purpose of this study was to develop an alternative method for the selective analysis of perchlorate with equal or better sensitivity than existing ion chromatography methods, which could be used for typical ground water samples.
SECTION II: METHODS AND MATERIALS

Test Materials and Reagents

Ammonium perchlorate [7790-98-9], acetonitrile [75-05-8], and glacial acetic acid [64-19-7] were purchased from Sigma-Aldrich Chemical Company. The mobile phase consisted of 0.5% acetic acid in acetonitrile. The stock perchlorate solution of 10 mg/ml perchlorate was prepared in distilled, deionized water gravimetrically from the ammonium salt of perchlorate.

Utah and Las Vegas Water Samples

In order to compare the electrospray mass spectrometric determination of perchlorate in ground water samples to the existing ion chromatographic techniques, two sets of real-life water samples were collected from the State of Utah and Nevada. Samples were collected and contributed by the State of Utah, Department of Environmental Quality Division of Solid and Hazardous Waste and Division of Drinking Water, Salt Lake City, Utah and the U.S. Environmental Protection Agency, National Exposure Research Laboratory, Las Vegas, Nevada. The Utah samples were collected from three different locations. All samples were ground water samples collected in duplicate, and containing TDS levels between the range of 300 to 800 ppm. Samples were run in the laboratory as unknowns at the time of analysis for perchlorate. Samples 4844-4847, 4836-4839 were collected from the Harkers Canyon alluvium which consists mostly of unconsolidated sand and gravel. The United States Geological Services (USGS) has identified this area of Salt Lake Valley as primary recharge. Samples 4834 and 4835 were obtained from the Coon Creek drainage, which is in the fault margin, situated along the toe of the Oquirr Mountains. Samples 4842 and 4843 were gathered from a blending point in a drinking water
system, which blends water from shallow artesian wells and deep pumped wells. The later samples were taken after chlorination.

The water used to prepare the Nevada study samples was collected in February 1998, from a well identified as 4 CP-1. The well is located on the Nevada Test Site (NTS). This well was selected because it was known to have been isolated from atmospheric and ground processes that contribute to the migration of surface compounds into the aquifer. The background tritium concentration in the raw water (< 2 pCi/L) is significantly lower than ground water which is recharged from surface sources, rain, and snow melt (> 30 pCi/L). Because of the long isolation of the water from processes likely to introduce perchlorate, it was unlikely that perchlorate would be present. Using the raw water from 4 CP-1, the study samples were prepared at three concentrations (C2, C3, C4) and three TDS levels (T1, T2, T3), in addition to sample C1, which was a blank at the three TDS levels, and a spiked distilled water sample, ST0. The concentration of perchlorate was 6, 18, and 36 parts per billion (ppb) for C2, C3, and C4 respectively and 51 ppb for ST0. Sample C1 was a blank. The TDS concentrations as a percent for T1, T2, and T3, were 25, 50, and 100 percent raw waters, respectively. The balance of the volume for T1 and T2 was distilled raw water.38

Extracted Reference Standards and Sample Preparation

Perchlorate standards at 0, 1, 5, 10, and 25, ng/ml were prepared in 2.5 ml distilled, deionized water by serial dilution from the stock (10 mg/ml) ammonium perchlorate solution. Samples were stored in a -25°C freezer and then an -86°C freezer for one hour each, in order to thoroughly freeze the samples. The frozen samples were then placed in a lyophilizer overnight, to remove the water and volatile contaminants at a low pressure and temperature, in order to avoid the loss of perchlorate. Following lyophilization, the samples were reconstituted in 1 ml
0.5% acetic acid/acetonitrile mobile phase. Prior to analysis by electrospray mass spectrometry, the reference standards were filtered with Millipore Millex-HV13 (0.45 μm) syringe filters.

For water samples collected from Salt Lake City, UT and Las Vegas, NV, 2.5 ml of the water was transferred to polypropylene test tubes without dilution. The samples were stored in a -25°C freezer and then an -86°C freezer for one hour each. The frozen samples were then lyophilized overnight. Following lyophilization, the samples were reconstituted in 1 ml 0.5% acetic acid/acetonitrile mobile phase and filtered with Millipore Millex-HV13 (0.45 μm) syringe filters. Samples were then analyzed using electrospray mass spectrometry. Unknown concentrations were found by comparing the peak area to the calibration curve generated from the lyophilized standards.

Unextracted Standards and Instrument Sensitivity Procedure

Unextracted Standards were prepared from the stock solution of 10 mg/ml perchlorate in distilled, deionized water. Stock solution was diluted serially without lyophilization in 0.5% acetic acid/acetonitrile mobile phase for final concentrations of 0.5, 1, 5, 10, 25, 50 and 100 ppb. Samples were then injected directly into the mass spectrometer. In order to monitor the sensitivity of the mass spectrometer, an unextracted standard curve was run at the start of each day. A signal to noise ratio of 3:1 or higher was required for the 0.5 ppb standard in order to continue with sample analysis.

Analytical Method

Electrospray mass spectrometry. Electrospray mass spectrometry was performed on a Finnigan-Mat TSQ 700 (San Jose, CA). A Harvard Apparatus (South Natick, MA) Model 22 syringe pump was used to deliver the mobile phase at a constant flow rate of 75 μl/min through an 82.5 cm x 1.14 mm I.D. Intramedic polyethylene tubing. The polyethylene tubing was
connected to the mass spectrometer by 22.3 cm of 0.10 μm I.D. fused silica capillary tubing. The heated capillary was set at 200°C, with an applied voltage of -10 V. The electrospray probe had an applied voltage of 5 kV. Nitrogen was used for the sheath gas, and was set at a pressure of 40 psi. The tube lens was set at -103 V.

The samples were injected directly into the electrospray mass spectrometer through a 10 μl sample loop. Samples were analyzed with the Finnigan ULTRIX 4.4 software. Mass Spectra were collected by scanning mass to charge ratios from 50 to 350, in a solution of 10 ppm ClO₄⁻ in 0.5% acetic acid/acetonitrile mobile phase. Perchlorate samples were selectively monitored at a mass to charge ratio of 99.1, using the negative ion MS mode. All other parameters were optimized for the detection of perchlorate by tuning the instrument specifically for perchlorate with a solution of 5 ppm perchlorate in 0.5% acetic acid/acetonitrile.

The method detection limit of the electrospray mass spectrometer was determined by the triplicate analysis of ten perchlorate standards at concentrations of 1 ppb. Percent Recovery was determined by 4 extracted standards for concentrations at both 5 and 25 ppb. The measured concentrations of the standards were found by comparing the peak area of the lyophilized standards to an unextracted standard curve.

Ion Chromatography. The results obtained by electrospray mass spectrometry were compared to that obtained on ion chromatography. All measurements using ion chromatograph studies (performed by Utah Health Lab and AFRL/HEST) were performed using a Dionex DX 500 ion chromatograph configured with a GP 40 gradient pump, CD 20 Conductivity Detector, and a AS-40 Automated sampler. Separation was obtained using a Dionex IonPac AS-11 analytical column and an AS-11 guard column. Anions were detected with suppressed conductivity detection using an ASRS ULTRA suppressor, an Anion Self-Regenerating
Suppressor. The eluent used was a 57% mM sodium hydroxide solution. All water used was de-ionized, reagent grade with 18 Ω-cm resistance. All samples were analyzed in duplicate in order to confirm analysis and assess matrix effect. A reagent water blank, reagent water blank fortified with known concentration of perchlorate, a sample fortified with known concentration of perchlorate, and standards at three different perchlorate concentrations were analyzed with the samples, in order to assure the quality of analysis.
SECTION III: RESULTS

Method Development and Validation

The mass spectrum of perchlorate in 1% acetic acid/acetonitrile (Figure 3.1) shows chlorinated peaks at 99.1, 140.1, and 159.12, which correspond to the ClO₄⁻ anion, and the CH₃CN-ClO₄⁻ and CH₃COOH-ClO₄⁻ adducts. The m+2 peaks at an abundance of 32.5% support the presence of chlorine.⁴⁷

Figure 3.1: Mass Spectrum of 10 μg/ml Perchlorate Solution in a 1% Acetic Acid/Acetonitrile Mobile Phase
Figure 3.2 shows the background spectrum for the mobile phase (1% acetic acid/acetonitrile). This background was subtracted from the perchlorate scan in order to show only the response to the ions that contain the perchlorate anion.

**Figure 3.2: Background Mass Spectrum for 1% Acetic Acid/Acetonitrile Mobile Phase Alone**

![Mass Spectrum](image)

The presence of perchlorate in the peaks at 99, 14, 159 was verified by the presence of these peaks after subtraction of the background spectrum in Figure 3.3. The presence of chlorine in the ions was also verified by the presence of m+2 isotope peaks at 32.5% abundance.\(^{47}\)
In order to obtain a calibration curve for the perchlorate samples, a series of standards were injected to the mass spectrometer (Figure 3.4). Results are obtained as selected ion current profiles (SICP), where each peak indicates an individual injection of a perchlorate standard. Calibration curves (Figure 3.5) were then obtained for perchlorate by plotting the peak area versus the known perchlorate concentration of the standards for the selected ion monitoring of m/z=99.1.

As shown in figures 3.4 and 3.5, a linear correlation was found between the peak area and the perchlorate standards from 0.5 to 100 ppb, with a correlation coefficient of 0.992. As a
result, the electrospray mass spectrometer was programmed to selectively monitor the mass to charge ratio of 99.1. The acetonitrile/perchlorate peaks and the acetic acid/perchlorate peaks did not show the same linear relationship between the detector response and the concentration of perchlorate.

**Figure 3.4: Typical Standard Curve for Unextracted Standards Monitored at a Mass to Charge Ratio of 99.1**
In order to determine the method detection limit (MDL) for lyophilized standards, ten samples at a concentration of 1 ppb were measured in triplicate. The method detection limit was determined according to EPA guidelines, with the following calculation:

$$\text{MDL} = (\text{stdev/mean}) \times \text{concentration} \times t$$  \hspace{1cm} (Equation 3.1)

Where the student t factor ($t$) = 2.602 for a 99% level of confidence and concentration = 1 ppb.

The method detection limit for lyophilized samples was calculated to be 0.38 ppb at a signal to noise ratio of 3 to 1. The reporting limit (RL) was found to be 1.15 ppb, with the calculation shown in Equation 2.

$$\text{RL} = 3 \times \text{MDL}$$  \hspace{1cm} (Equation 3.2)

The instrument detection level (ID) represents the sensitivity of the instrument being used for analysis toward the compound of interest. The use of the instrument detection level provides a basis for the comparison of the sensitivity of different instruments for the same compound. The
instrument detection limit was found to be 3.8 ppb, with equation 3.3, where V is the volume of the sample injected for analysis.

\[ \text{ID} = \text{MDL} \times V \quad \text{ (Equation 3.3)} \]

The percent recovery for the method was determined with samples at concentrations of 5 and 25 ppb. The average percent recovery was calculated to be 82.4% with the following equation:

\[ \% \text{ Recovery} = \frac{(C_s - C)}{S} \times 100 \quad \text{ (Equation 3.4)} \]

where \( C_s \) = measured concentration of the standard, \( C \) = measured concentration of the blank, and \( S \) = known concentration of the standard. The percent recovery for the method is acceptable within +/- 20% of one hundred percent recovery.

Results from the collaborative study performed on Las Vegas drinking water are shown in Table 3.1. Samples are listed in order of increasing concentration of total dissolved solid (TDS). The water samples with low levels of TDS agree with the collaborative ion chromatography results within the acceptable variance of +/- 20%. Only one sample (sample number 12) is outside of the acceptable range by 8%. 

16
Table 3.1: Nevada Ground Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>TDS (ppm)</th>
<th>TSQ (ppb)</th>
<th>IC (ppb)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>49.4</td>
<td>51</td>
<td>97%</td>
</tr>
<tr>
<td>2</td>
<td>71</td>
<td>0</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>71</td>
<td>0</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>4</td>
<td>71</td>
<td>0</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>5</td>
<td>142</td>
<td>4.4</td>
<td>5</td>
<td>88%</td>
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<td>142</td>
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<td>282</td>
<td>15.8</td>
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<td>282</td>
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<td>12</td>
<td>282</td>
<td>21.0</td>
<td>29</td>
<td>72%</td>
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The results for the Utah ground water samples are listed in Table 3.2, in order of increasing concentration of TDS. Again, samples with low levels of TDS show agreement between electrospray mass spectrometric analysis, and the ion chromatography analysis performed by AFRL. However, as the concentration of total dissolved solid increases, the variance between the two methods also increases.
Table 3.2: Utah Ground Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>TDS (ppm)</th>
<th>TSQ (ppb)</th>
<th>IC (ppb)</th>
<th>%Recovery</th>
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<td>319</td>
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<td>4843</td>
<td>766</td>
<td>6.3</td>
<td>15.6</td>
<td>40%</td>
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SECTION IV: DISCUSSION AND CONCLUSIONS

Electrospray mass spectrometry is a viable method for the determination of perchlorate in drinking water and ground water. This method has demonstrated greater selectivity and sensitivity for the analysis of perchlorate than existing ion chromatography methods. The ability of electrospray mass spectrometry to selectively monitor the perchlorate anion results in a method that is more selective for perchlorate than the current ion chromatography method, which relies on retention time to identify perchlorate. Furthermore, analysis by electrospray mass spectrometry shows a higher sensitivity than that of the current accepted IC method. Intra-laboratory studies have shown the method detection limit for the electrospray mass spectrometric determination of perchlorate to be 0.38 ppb, while current ion chromatography techniques have an accepted method detection limit of 4 parts per billion. Electrospray mass spectrometry increases the current level of detection by an order of magnitude. The sensitivity of electrospray mass spectrometry toward perchlorate analysis shows an improvement of more than three orders of magnitude over the current ion chromatography method, which requires a 1000 ml injection volume. The instrument detection level for electrospray mass spectrometry was calculated to be 3.8 ppb, which is a significant improvement over the accepted ID of 4000 ppb for ion chromatography.

This method can also be used to successfully quantitatively detect perchlorate in real world drinking water and ground water. Inter-laboratory studies performed on ground water samples obtained from both Utah and Las Vegas water supplies demonstrated the ability of electrospray mass spectrometry to accurately determine the amount of perchlorate present in water samples with typical levels of total dissolved solid. Electrospray mass spectrometric results for typical water samples with TDS concentrations of less than 700 ppm were within +/-
20% of corresponding ion chromatography results. However, samples with unusually high levels of total dissolved solid showed a significant variance from values obtained through ion chromatography. Samples with TDS levels greater than 700 ppm showed a difference of 60-70% from the corresponding ion chromatography values.

Especially high levels of total dissolved solid interfere with both ion chromatography and electrospray mass spectrometry. High TDS levels interfere with the signal to the conductivity detector that is used with ion chromatography. In the mass spectrometer, the dissolved solid in particularly dirty water samples can plate out on the heated capillary. This can cause both difficulties in cleaning the instrument and capillary failure. Capillary failure causes an increased background noise and inaccurate quantitation. It is also possible for the large concentration of interference anions to overwhelm the quadrupoles. Consequently, more interference anions reach the detector, and the background noise is significantly increased. The increase in background noise within the detector results in decreased sensitivity and less accurate determination of perchlorate concentrations. It is necessary, then, to develop a sample preparation method which would effectively remove high concentrations of dissolved solids from exceptionally dirty water samples without interfering with the analysis of perchlorate.

AFRL/HEST is in the process of developing a sample preparation method for use with both electrospray mass spectrometry, and the current ion chromatography methods. The sample preparation method involves the use of a cation exchange resin. Silver cations are allowed to exchange onto the resin before introducing the sample. Passing the water sample through the resin allows the less soluble silver salts of the interference anions to precipitate out. However, perchlorate stays in solution due to the high solubility of silver perchlorate. The development of
this method, which will allow the analysis of perchlorate in water with high levels of total dissolved solids, will be described in a subsequent technical report.
SECTION V: REFERENCES

1. Las Vegas Sun, September 23, 1997
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SECTION VI: ACKNOWLEDGEMENTS

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