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Introduction

Investigations into the occurrence and origin of perchlorate (ClO_4^-) found in groundwater from across North America have been sparse until recent years, and there is mounting evidence that natural formation mechanisms are important (Fram and Belitz, 2011; Jackson et al., 2010; Parker et al., 2008; Parker et al., 2009; Plummer et al., 2006; Rajogopalan et al., 2006; Rao et al., 2007). New opportunities for identifying groundwater perchlorate and its origin have arisen with the utilization of improved detection methods (Koester et al., 2000) and sampling techniques (Brown et al., 2001; Gu et al., 2001; Bao and Gu, 2004). Additionally, application of the forensic potential of isotopic measurements has begun to elucidate sources, potential formation mechanisms and natural attenuation processes (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006; Sturchio et al., 2009; Jackson et al., 2010; Slaten et al., 2010; Sturchio et al., 2011; Sturchio et al., 2003; Sturchio et al., 2007; Hatzinger et al., 2009; Coates and Achenbach, 2004).

Isotopic compositions of natural perchlorates

Advances in technologies needed to capture, purify, and analyze isotopic composition of groundwater perchlorate were presented by Bao and Gu (2004) based on earlier research performed at Oak Ridge National Laboratory and the University of Tennessee - Knoxville (Brown et al., 2001; Gu et al., 2001; Brown et al., 2002). Bao and Gu (2004) utilized a new perchlorate-selective anion-exchange resin (commercially sold, as product #: A530E, by Purolite Corp., Bala Cynwyd, Pennsylvania, USA) to collect quantities of perchlorate needed for isotopic analysis. The resin's high selectivity for perchlorate together with additional purification steps allows separation of perchlorate from co-associated oxy-anions and chlorine during elution enables compound specific isotope measurements in water samples containing perchlorate to the tens or hundreds of ppb level. With this approach (detailed below), also advanced by J.K. Böhlke (USGS) and his collaborators (N.C. Sturchio, W.A. Jackson, P.B. Hatzinger), the isotopic composition and origin of natural perchlorates began to be explored.

Bao and Gu (2004) reported that nitrate ore from the Atacama Desert caliche (described by Ericksen, 1983) in Chile contained perchlorate with positive $\Delta 17\text{O}$ (i.e., $\Delta 17\text{O} = (\delta 17\text{O} - 0.52(\delta 18\text{O}))$) values (see Table 1), in agreement with the positive $\Delta 17\text{O}$ values for the co-situated sulfate and nitrate salts determined by Michalski et al. (2004). This 17O excess (i.e., above levels that could be explained by mass dependent fractionation alone (i.e., $\delta 17\text{O} > 0.52 \delta 18\text{O}$) of perchlorate was considered by Bao and Gu to be determinative of ozone oxygen incorporation (ozone O_3 $\Delta 17\text{O} \sim 20$ to 50‰ ; Thiemens and Heidenreich, 1983; Thiemens 1999) into perchlorate during its formation in the stratosphere. Anthropogenic (i.e., synthetic) perchlorate shows only mass dependent 17O fractionation (i.e., $\Delta 17\text{O} \sim 0 \text{‰}$; see Table 1), which is indicative of terrestrially-derived materials since atmospheric- and water- O_2 have $17\text{O} \sim 0 \text{‰}$. Bao and Gu (2004) concluded that an unambiguous signature for naturally-formed perchlorate had been discovered.

A significant advantage in using the derived value, $\Delta 17\text{O}$, for perchlorate forensics is that it is conserved despite any post-depositional isotopic transformations governed by kinetic and equilibrium isotope fractionation. This led to field investigations of sites with known perchlorate contamination utilizing Bao and Gu's interpretation of 17O abundance to apportion the perchlorate's origin (Sturchio et al., 2005; Böhlke et al., 2009; Slaten et al., 2010; Sturchio et al., 2011). These investigations combined knowledge of perchlorate's isotopic composition with additional chemical (e.g., major and minor ions, CFCs, VOCs, TOC, dissolved O_2), isotopic (e.g., $3\text{H}/3\text{He}$, 2H), and

hydrological (e.g., groundwater modeling, transect wells) evidence to assign perchlorate as either from 1) contamination from agricultural (or horticultural) application of Chilean nitrate ore-bearing fertilizers (e.g., Urbansky et al., 2001), or 2) contamination from release of industrially-derived synthetic perchlorate.

A consistent association of natural perchlorate with mass-independent $\Delta 17\text{O}$ fractionation, as per Bao and Gu (2004), is now questioned after isotopic investigations by Jackson et al. (2010) of the putatively natural perchlorate commonly found in groundwater (e.g., Dasgupta et al., 2005; Plummer et al., 2006; Rajagopalan et al., 2006) and associated subsurface unsaturated zones (e.g., Rao et al., 2007) of the southwestern United States (i.e., Southern High Plains, Texas; Rio Grande River Basin, New Mexico). The natural perchlorates here do not possess a significant mass-independent $\Delta 17\text{O}$ fractionation and had relatively higher $\delta 37\text{Cl}$ and $\delta 18\text{O}$ values than the aforementioned Atacama Desert perchlorate (Table 1). Thus, a stratospheric origin, as per Bao and Gu (2004), for these perchlorates is not substantiated. Jackson et al. (2010), investigating other possible sources of this perchlorate, discovered that the clay-hill nitrate caliche of the nearby (~ 1200 km) Mojave Desert (California, USA), described by Noble and Mansfield (1922), contained perchlorate with substantial mass-independent $\Delta 17\text{O}$ fractionation. In fact, the Mojave Desert caliche had $\Delta 17\text{O}$ levels even higher than those observed for the perchlorate found in Atacama Desert caliche (Table 1). Sturchio et al. (2009) reported substantial quantities of the cosmogenic radionuclide ^{36}Cl in the North American perchlorates (Table 1), which further complicates any easy interpretations regarding their origin. The presence of ^{36}Cl in perchlorate indicates an atmospheric or near-surface origin given that most natural ^{36}Cl is produced in the upper atmosphere by cosmic activation of argon, subsequently falling to the Earth in rainwater. The North American perchlorates investigated have higher levels of $^{36}\text{Cl}/\text{Cl}$ indicating more recent fallout and accumulation, given that the Atacama deposits are old enough for most ^{36}Cl to have decayed away. Other data, for example the co-occurrence of iodine (Dasgupta et al., 2005), indicates an atmospheric origin for the southwestern United States perchlorate. Unfortunately, these data do not reconcile the observed inconsistent presence of mass-independent $\Delta 17\text{O}$ fractionation for perchlorates across the North American sites. To explain this, Jackson et al. (2010) commented that there may be an as yet unknown and possibly catalyzed post-depositional isotope exchange involving perchlorate's oxygen even if perchlorate's oxygen is considered to be quite stable in water (Hoering, 1958). Alternatively, Jackson et al. (2010) rationalized that multiple perchlorate formation mechanisms may exist globally with variations in precursor compound isotopic composition. The cause of these geographical isotopic differences (i.e., southwestern USA \leftrightarrow Mojave Desert \leftrightarrow Atacama Desert, see Table 1) in natural perchlorate remains unknown.

Knowledge of natural perchlorate's isotopic composition, although resulting so far in only incomplete understanding of perchlorate's origin(s), was made possible by significant advances in analytical techniques. The purity requirements for the final perchlorate sample obtained for analysis demand contamination removal to levels substantially below the differences observed in the purported source materials' isotopic abundances. The available method, described in detail below, has been used to discern isotopic differences among perchlorates (Table 1) of at least 7.1 ‰ (Mojave- vs. Atacama- caliche) in $\delta 18\text{O}$, 8 ‰ (synthetic vs. Atacama caliche) in $\Delta 17\text{O}$, 6.8 ‰ (synthetic vs. Atacama caliche) in $\delta 37\text{Cl}$, and $\sim 50 \times 10^{-15}$ (synthetic vs. Atacama caliche) in $^{36}\text{Cl}/\text{Cl}$. For stable isotopic analyses, this is a remarkable analytical achievement given that the contaminating nitrate salts are co-situated at much higher abundances (e.g., 6.3%) in mineral caliche than the trace levels of perchlorate (e.g., 0.03%) (Grossling and Ericksen, 1971). Analytical precision of replicate samples and standards are reported to be at least 1 ‰ for $\delta 18\text{O}$, $\Delta 17\text{O}$, $\delta 37\text{Cl}$ (e.g., Jackson et al., 2010; Sturchio et al., 2005).

The extent to which a method can discern the isotopic differences among the perchlorate sources reported in Table 1 will depend on the amount of sample available, the sample's representativeness, the purity level and isotopic composition of interfering chlorine- and oxygen- contamination, and the accuracy and precision of the analysis. Regarding purity requirements, with 50 μmol of sample perchlorate, the presence of only 50 nmol of chloride or 200 nmol of oxy-anion oxygen would

contribute 1 ‰ contamination. This could lead to an up to 1 ‰ deviation from the true perchlorate isotopic composition from contamination (assuming a simple two component mixing model involving the perchlorate and its contaminants, substantially composed of one end-member). Smaller perchlorate sample sizes, for example as might be obtained from low concentration groundwaters, will result in smaller tolerable contamination levels. Ideally, the method for obtaining perchlorate should be able to tolerate the sample size required, remove and not contribute oxygen- or chlorine-contamination, and not result in any isotopic fractionation.

Table 1. Range of isotopic abundances reported for natural and synthetic perchlorates.

Perchlorate Type	N	ClO ₄ ⁻ δ18O, ‰	ClO ₄ ⁻ Δ17O, ‰	ClO ₄ ⁻ δ37Cl, ‰	ClO ₄ ⁻ 36Cl/ Cl, (10 ⁻¹⁵)	Reference
Atacama caliche	1	NA	NA	NA	22±3 to 590±20	Sturchio et al., 2009
	4	-9.3 to -4.2	+8.93 to +9.57	-14.5 to -11.8	NA	Sturchio et al., 2006
	5	-10.5 to -5.2	+8.1 to +9.4	-14.3 to -11.8	NA	Jackson et al., 2010
Atacama groundwater	1	-7.6	+9.3	-12.9	NA	Jackson et al., 2010
Mojave caliche	1	NA	NA	-1.4	19200±890	Sturchio et al., 2009
	4	+2.9 to +26.1	+8.6 to +18.4	-3.7 to -0.81	NA	Jackson et al., 2010
Synthetic	20	-24.8 to -13.5	-0.04 to +0.12	-3.1 to +1.6	NA	Sturchio et al., 2006
	17	NA	NA	-5.0 to +1.6	0±2.5 to 34±2	Sturchio et al., 2009
	14	NA	NA	NA	4 to 155	Hillegonds et al., 2008
SW USA unsaturated zone	1	+2.1	+0.8	+3.7	NA	Jackson et al., 2010
SW USA groundwater	7	NA	NA	NA	3130±100 to	Sturchio et al., 2009
	10	+0.55 to +4.8	+0.2 to +1.3	+3.1 to +5.1	28800 ±920	Jackson et al., 2010

Review of the available method for isotope forensics of groundwater perchlorate

Since natural perchlorate in groundwater (≤10 nM) coexists with abundant (~10 μM to 300 μM) oxy-anion species (e.g., SO₄²⁻, NO₃⁻), chloride (Cl⁻) and dissolved organic matter (30-50% oxygen), the analytical method for perchlorate isotope forensics, will need to efficiently concentrate perchlorate and substantially remove these nuisance substances before isotopic analysis can proceed. The available method (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2009) that could be utilized is described in sequence below together with any special analytical challenges for low concentration natural perchlorate from groundwater. The widespread and putatively natural perchlorate found in groundwater is typically at low levels for locations across the coterminous North America (e.g., Fram and Belitz, 2011, Plummer et al., 2006; Parker et al., 2008; Parker et al., 2009; Urbansky, 1998). Forensic analysis of groundwater perchlorates have so far focused on either industrially or agriculturally contaminated sites (e.g., Böhlke et al., 2009; Slaten et al., 2010; Sturchio et al., 2011) or sites with unusually high levels of natural perchlorate (e.g., 200 to 600 nM ClO₄⁻; Jackson et al., 2004).

Perchlorate-selective anion-exchange resin (A530E, Purolite Corp., Bala Cynwyd, Pennsylvania, USA) packed into columns (typical resin bed volume (BV) = 100 mL) is used to concentrate groundwater perchlorate by pumping the water through the resin bed (Jackson et al., 2010). Normal filtering of the sample is necessary to avoid particulate matter. A minimum of 5 mg (i.e., 50 μmol) of perchlorate is required for analysis, but higher amounts (e.g., 10 to 80 mg, Sturchio et al., 2007) have been more commonly collected, the higher amounts likely associated with groundwater containing higher perchlorate concentration. Higher amounts of perchlorate recovery will allow more confident sample handling and replication. The minimum perchlorate requirement (i.e., 50 μmol) of this method necessitates at least 5,000 liters of typical (i.e., ≤10 nM) groundwater to be processed through the resin column creating a substantial time burden for field work. The sampling apparatus (BV = 100 mL) is capable of loading perchlorate, without breakthrough, at flow rates of up to 2 L/

min (Jackson et al., 2010); thus, requiring at least 1.75 days to load the 100-mL column with the required perchlorate.

After perchlorate capture, the ClO_4^- laden resin is rinsed with 3 bed volumes (BV) of 4 M hydrochloric acid (HCl) to remove more weakly sorbing anions (e.g., SO_4^{2-} , NO_3^-) and possibly other impurities (e.g., low molecular weight organic acids). Details of the removal of any contaminants have not been provided in any of the published works describing the available method (e.g., Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2009; Jackson et al., 2010). The sorbed ClO_4^- is then eluted from the column using 3 to 5 BVs of a mixed solution of 1 M FeCl_3 and 4 M HCl (Jackson et al., 2010). Complete perchlorate elution is desirable in order to minimize any perchlorate fractionation. Perchlorate recoveries of >95% are reported to be easily achievable (e.g., Bao and Gu, 2004; Jackson et al., 2010). An organic solvent (e.g., 35% (v/v) ethanol) miscible in the ferric chloride solution for adjusting its ionic strength and polarity has been mentioned for maximizing the efficiency of the perchlorate displacement from the anion-exchange resin (Brown et al., 2002), but this step does not seem to be a requirement since it has been inconsistently mentioned. For the acidic ferric chloride eluent, the displacing anion is identified as tetrachloroferrate, FeCl_4^- (Gu et al., 2001). Other eluents are possible (e.g., salicylate or tetrafluoroborate (BF_4^-); Brown et al., 2002), but only the ferric chloride eluent has been adopted for desorption of perchlorate from the A530E resin for forensic studies. With the latter eluent, significant quantities of potentially-contaminating chlorine (i.e., 7 M Cl as chloride) are introduced to the sample. The total quantity of chlorine requiring removal is dependent upon the resin bed volume and number of eluent bed volumes needed for complete perchlorate elution. Larger resin bed volumes, for example for reducing hydraulic limitations and increasing groundwater processing rates, lead to increased eluent-derived chlorine that will need to be removed from the final perchlorate sample.

After resin desorption, the perchlorate-bearing eluent is neutralized with a strong base, 5 M NaOH, to a pH of between 9 and 10, which results in the precipitation of the ferric iron as $\text{Fe}(\text{OH})_3$ (Jackson et al., 2010). The resulting suspension is centrifuged and the clear supernatant (containing dissolved ClO_4^-) is collected. Perchlorate and other displaced anions may partially or completely sorb on and/or co-precipitate with the iron oxyhydroxides and so these are thoroughly washed with DI water and the supernatants are then combined and concentrated to achieve a final ClO_4^- concentration of at least 0.05 M (Jackson et al., 2010).

The high (0.05 M) perchlorate concentration in the final product water is needed for gravimetric precipitation used in separating the perchlorate from its contaminants. Perchlorate, once at this concentration, is precipitated as an alkaline metal perchlorate (e.g., CsClO_4 by addition of a precipitating agent, e.g., CsCl or CsOH) (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2009; Jackson et al., 2010). Although perchlorate precipitation may be useful in some cases for nuisance groundwater contaminant removal, the alkali metal perchlorates have high enough solubilities (i.e., ~0.1 M) that it will be a challenge generating enough perchlorate for precipitation from typical groundwaters (≤ 10 nM ClO_4^-). Evapoconcentration of the resin-desorbed perchlorate will require substantial volume reduction (e.g., 50 μmol of perchlorate recovered in 500 mL eluate must have its volume reduced 500-fold) that could make sample handling and precipitation impractical. These problems will be exacerbated when using KClO_4 due to its higher solubility (versus CsClO_4 or RbClO_4), and at the high ionic strengths created by chloride additions (e.g., 7 M Cl⁻ is used in the eluent) (von Kiparski, Parker 2010, unpublished data). Incomplete precipitation of the perchlorate is a concern since it could lead to isotopic fractionation (e.g., heavier isotopes precipitating preferentially). In addition, a colloidal suspension could form after adding the precipitating agent making perchlorate recovery by filtration difficult.

The alkaline perchlorate solids (precipitated as either CsClO_4 , RbClO_4 , KClO_4 ; e.g., Bao and Gu, 2004; Böhlke et al., 2005) are then filtered and rinsed with a few drops of 90% methanol, and their purity is verified by micro-Raman spectroscopic analysis (Bao and Gu, 2004; Jackson et al., 2010). Residual chlorine (as Cl⁻) contamination introduced by the acidic ferric chloride solution is apparently removed during this washing step, but no details of these results are given. If sulfate or nitrate is

detected (via scattering at their characteristic Raman bands of $\sim 1050\text{ cm}^{-1}$ and $\sim 994\text{ cm}^{-1}$, respectively), the samples are resuspended and reprocessed until they are deemed free of these impurities based on subsequent micro-Raman analyses. The reprocessing steps for purification, described by Sturchio et al., 2007 as “additional cation exchange, oxidation, and evaporation steps”, are not explicit enough to document here, or to reproduce their published results.

Additional checks on the overall success of the above-described perchlorate purification procedures are conducted using reference standards with known isotopic compositions (e.g., USGS37 and USGS38, see Jackson et al., 2010; these two standards are available from T.B. Coplen at USGS-Reston). The standards are analyzed for isotopic composition before and after being dissolved, captured, extracted, precipitated, and purified. Using the above-described procedures, no significant isotopic fractionation has been reported indicating the robustness of the method.

The alkaline metal perchlorate produced by precipitation as described above is next prepared for oxygen isotope determination. In analyzing $\delta 180$, typically CO_2 or CO are used, but for $\Delta 170$ measurements O_2 is required because of isobaric interference of the ^{13}C at m/z 45 ($^{16}\text{O}^{13}\text{C}^{16}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{17}\text{O}$). To produce O_2 , an aliquot of the alkaline metal perchlorate (e.g., CsClO_4) is thermally decomposed at $650\text{ }^\circ\text{C}$ (for CsClO_4) for ~ 12 to 30 min for $\delta 180$ and $\delta 170$ analysis. The decomposition is conducted using an off-line evacuated-quartz tube containing the perchlorate crystals (often sealed in silver capsules) followed by dual-inlet isotope ratio mass spectrometry on the generated O_2 at m/z 32, 33, and 34 (Bao and Gu, 2004; Böhlke et al., 2005). The decomposition gases are passed through and expanded in liquid N_2 traps directly to the dual-inlet interface. For duplicate samples, the difference in $\delta 180$ values is reported to be less than $1.0\text{ }‰$. Duplicate $\Delta 170$ values are reported to be within $0.1\text{ }‰$ (1σ) based on replicate analysis of samples and isotopic reference materials. The small deviation in $\Delta 170$ values is explained as representing a small covariation of $\delta 180$ and $\delta 170$ arising during the analytical procedures. Oxygen isotope compositions are calibrated against the oxygen isotope standard, V-SMOW ($\delta 180 = 0.00\text{ }‰$; Coplen et al., 2002). Yields of O (as O_2), not reported, are typically within 5% for perchlorate reagents, samples and measured aliquots of tank O_2 (Böhlke et al., 2005). Mass-independent 170 fractionation (i.e., $\Delta 170$) was assumed to be $0\text{ }‰$ for the representative synthetic KClO_4 reagent designated USGS37 (Böhlke et al., 2005), which is consistent with the derivation of O from H_2O during ClO_4^- synthesis. Because of the way $\Delta 170$ is derived, there is no dependence of $\Delta 170$ values on O yield.

The chloride residue from the decomposed ClO_4^- salt is analyzed for $\delta 37\text{Cl}$ after conversion to CH_3Cl for $\delta 37\text{Cl}$ analysis according to established methods (Böhlke et al., 2005) (for details of these established methods see Taylor and Grimsrud 1969; Long et al., 1993; Eggenkamp 1994, Holt et al., 1997). In brief, the alkali chloride salt produced by ClO_4^- decomposition is first dissolved in warm Type I water and then the Cl^- is precipitated as AgCl by addition of AgNO_3 (Böhlke et al., 2005). The method for chlorine isotope analysis with IRMS requires chlorine in the sample to be converted to silver chloride. The AgCl is protected from photodissociation by storing it in darkness after formation. The recovered and dried AgCl is then reacted in a sealed borosilicate glass tube with a stoichiometric excess of iodomethane (CH_3I) at $300\text{ }^\circ\text{C}$ for 2 h to produce CH_3Cl , which is purified cryogenically and then analyzed in dual-inlet mode by measurements at m/z 50 ($\text{CH}_3^{35}\text{Cl}^+$) and 52 ($\text{CH}_3^{37}\text{Cl}^+$) using isotope ratio mass spectrometry. Analytical chlorine yields of this procedure for reagent salts are reported as 81 to 97% with no significant dependence of isotope ratio on yield (Böhlke et al., 2005). The average reproducibility of $\delta 37\text{Cl}$ values is $\pm 0.3\text{ }‰$ (1σ) based on replicate analysis of samples and isotopic reference materials. Chlorine isotope compositions are calibrated against the chlorine isotope standard, SMOC ($\delta 37\text{Cl} = 0.00\text{ }‰$; Coplen et al., 2002).

Samples are analyzed for ^{36}Cl abundance by accelerator mass spectrometry (AMS) (Sturchio et al., 2009). The method requires chlorine in the sample to be precipitated as silver chloride with a molar excess of silver (Ag^+) as silver nitrate. Sulfur (^{36}S) (principally as sulfate) contamination is a known and significant interference for ^{36}Cl determination with AMS. Barium nitrate can be added to precipitate the sulfur contamination as barium sulfate at a basic pH. The barium sulfate can be

filtered away followed by re-precipitation of Cl⁻ as AgCl with acidification. Our results for synthetic perchlorate salt analysis via AMS, summarized in Table 1 and explicitly shown in Table 2 demonstrate the precision of the Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry, in which the stable chlorine isotope ratios are reproducible to 0.1 to 0.4 percent. AMS measured ³⁶Cl/³⁷Cl ratio uncertainty depend mainly on ³⁶Cl content and the consequent counting statistics, with replicate and single measurement uncertainties being similar for higher level samples which have coefficients of variation is between 3 and 11%. Samples measured more than once demonstrate that there is clear differentiation in ³⁶Cl/³⁷Cl. AMS measurements of stable ratios also demonstrate differences among salts, but the replicate precision of up to 0.4% is a limitation of AMS for stable isotope ratio measurements.

Table 2. LLNL analyses for synthetic perchlorates via AMS.

Lab ID	Salt	N	³⁶ Cl/ ³⁷ Cl (10 ¹⁵)	% CV	δ ³⁷ Cl, ‰
-- replicate analyses --					
salt 1	KClO ₄	5	130±10	11	-2±3
salt 3	KClO ₄	5	26±4	16	0.9±2
salt 12	Mg(ClO ₄) ₂	5	8±4	54	6±1
salt 13	NH ₄ ClO ₄	5	132±4	3	-0.8±4
Blanks	chloride	2	4.7±0.7	14	-0.1±2
-- single analyses --					
Salt 5	NaClO ₄	1	134±4	4	-2
Salt 5	NaClO ₄	1	134±4	4	-2
Salt 6	NaClO ₄	1	130±4	4	-4
Salt 8	NaClO ₄	1	102±3	3	-4
Salt 9	NaClO ₄	1	140±6	4	-2
Salt 11	Mg(ClO ₄) ₂	1	121±4	3	-5
Salt 14	Ca(ClO ₄) ₂	1	116±6	5	19
Salt 15	Ca(ClO ₄) ₂	1	120±9	7	11
Salt 16	Cd(ClO ₄) ₂	1	120±10	9	4
Salt 17	NiClO ₄	1	117±6	5	6
Salt 18	Zn(ClO ₄) ₂	1	127±7	5	-0.1

Given that the chemistry associated with chlorine-only measurements is significantly more simple than that for oxygen isotopes, mainly due to a lack of chlorine contamination versus oxygen, we have developed a simplified method for perchlorate chlorine analysis. Further development is underway to fine-tune this method for oxygen isotopes.

Silver perchlorate freeze drying method

We have developed a new method, using silver oxide addition and freeze-drying, obtaining AgClO₄ as the target compound for perchlorate isotope forensics that avoids the inherent difficulties associated with gravimetric precipitation in the previously published method. We feel that our method is more suitable for investigating the origin of dilute-, putatively natural- groundwater perchlorates using isotope (δ¹⁸O, Δ¹⁷O, δ³⁷Cl, ³⁶Cl/Cl) analyses. Our underlying premise is that perchlorate can be trapped on highly selective anion-exchange resin (i.e., A530E, Purolite Corp., Bala Cynwyd, PA, USA), rid of contaminating oxyanions and dissolved organic matter (DOM), and desorbed with acidic ferric chloride (1 M FeCl₃ 4 M HCl) eluent using the procedures developed by Bao and Gu (2004). In our method, the final solution containing ClO₄⁻ is neutralized using high-purity Ag₂O to quantitatively remove the contaminating chloride. The resulting solution should contain only Ag⁺ and ClO₄⁻, which can then be freeze-dried for subsequent isotopic analysis. The method is similar to procedures developed by Silva et al. (2000) for preparing nitrate for isotopic analysis. The advantages of our

method are as follows: (1) recovery of ClO_4^- from solution in silver-form by Ag_2O addition uses freeze drying and, thus, avoids any precipitation requirement, which is an advantage when only small quantities ClO_4^- are available, (2) the recovery of ClO_4^- in silver-form, takes advantage of the high solubility of AgClO_4 with respect to its primary chlorine contaminant, chloride, which is easy to precipitate quantitatively, (3) Chlorine residue resulting from the combustion of sample material (AgClO_4) for oxygen isotope analysis is conveniently in the form used (AgCl) for ^{36}Cl analysis with no aqueous conversion step involved as is the case in the available method, (4) as per (3), the sample chlorine, as AgCl , is conveniently in the form necessary for conversion to CH_3Cl for $\delta^{37}\text{Cl}$ analysis with no aqueous conversion step involved, (5) the method is well-suited for isotope dilution methods since very small quantities (e.g., 40 to 100 ng ClO_4^-) of perchlorate can be recovered and purified.

Our method requires meticulous wash steps to avoid contamination of the perchlorate with its isotopic interferences: chloride, the oxy-anions (e.g., nitrate and sulfate) and DOM. These sources of contamination are in groundwater, but may also arise during synthesis of the AgClO_4 depending on the amount of contamination introduced by the associated reagents (i.e., Ag_2O , FeCl_3), ion-exchange resin, and container surfaces (e.g., rotary evaporator flasks, transfer flasks). In the experiments below, we detail the significance of different sources of isotopic interference when using our method and describe procedures for their reduction or elimination. Procedures for thermal decomposition of AgClO_4 to O_2 and to chloride (as AgCl) together with

Experimental Procedures

Reagents and materials

All reagents used were ACS certified purity or better, and solutions were prepared using type I water. Ferric chloride was from Fisher Scientific (Hampton, NH, USA) (Ferric Chloride Hexahydrate, certified ACS, Cat.#: I88-500, Lot #: 093154), HCl from Fisher Scientific (HCl, trace metal grade, Cat.#: A508-212, Lot #: 4108100), AgClO_4 from MV Laboratories (Silver Perchlorate Monohydrate, 99.999%, AG490, Lot #: P403AGA1), and Ag_2O from Alfa Aesar (Silver Oxide, Cat.#: 11407, Lot #:G28T033).

Bulk as-received silver oxide (Ag_2O) powder often contains residual nitrate contamination (e.g., Silva et al., 2000). The silver oxide also may contain silver carbonate, likely from absorption of carbon dioxide (e.g., Barnes et al., 1971), but carbonates were never detected in final product water and so are not addressed here. We washed our batch of Ag_2O , obtained from Alfa Aesar, with agitation using Type I water (m:v = 1:20). After each wash cycle (~24 h), the silver oxide powder's NO_3^- contamination was measured after reducing the mixture's volume (final m:v = 1:4) by decanting the solution and equilibrating the resulting mixture for 1 h. These steps were taken in order to increase the sensitivity of the nitrate test. Nitrate determination of the solution was performed using either nitrate test strips (Aquacheck, Hach Chemical Co., Loveland, CO, USA), colorimetry (Low Range Test Kit, Model NI-14, Hach Chemical Co., Loveland, CO, USA), or ion chromatography (described below). In our silver oxide, nitrate contamination was progressively reduced from 1 mmol NO_3^- / kg Ag_2O to less than 2.6 $\mu\text{mol NO}_3^-$ / kg Ag_2O over 38 water bath changes and 1664 h total agitation time. The latter washed Ag_2O was used to obtain our highest -purity perchlorate.

After washing the Ag_2O powder, it is heated to $T = 170\text{ }^\circ\text{C}$ for 24 h in order to dry it and remove Ag_2O -associated DOM contamination (rationale for the latter was obtained by experiment 4 below).

Washing of laboratory glassware and plasticware

All glassware and plasticware used in preparing the purified perchlorate were washed and thoroughly rinsed using protocols to minimize chlorine- and oxygen- contamination. We used a 1 M acetic acid bath (as an alternative to an HCl bath) to remove chlorine from container surfaces before the final Type 1 water rinse step, and all glassware was prepared by heating to $400\text{ }^\circ\text{C}$ for 24 h.

Loading and extraction of perchlorate from the anion-exchange resin

Perchlorate trapping anion-exchange resin (A530E, Purolite Corp., Bala Cynwyd, PA, USA) and acidic ferric chloride (1 M FeCl₃ and 4 M HCl) eluent for perchlorate desorption were identical to those developed by others (see Brown et al., 2001; Gu et al., 2001; Brown et al., 2002; Bao and Gu (2004)) and used for perchlorate recovery from groundwater (e.g., Jackson et al., 2010). The as-received A530E resin is rinsed in Type 1 water for 48 h in a beaker with agitation in order to hydrate the resin before packing it into the sampling column for field use.

A field sampling apparatus was fabricated for capturing perchlorate (see *Supplementary Information* for schematic and parts list). With this sampling equipment, we sought to obtain a rugged, field-deployable column for capturing perchlorate from groundwater. The column was constructed from standard, hardware-store 1/2 x 6" brass nipple (1.5 cm ID x 15 cm length; resin total bed volume ~ 25 mL) fitted with hose-barb fittings on the endcaps, and two small screens to confine the anion-exchange resin. The field-sampling apparatus was tested for any hydraulic limitations present after loading it with resin (BV= 20 mL). When loading the column with resin amounts below the full BV capacity, glass wool was placed into the void space in order to prevent turbulent and bypass flow. In the main, flow rates up to 500 mL/ min through the field-deployable column were only slightly diminished by the presence of the resin (as compared to unrestricted flow) indicating no hydraulic limitations to our column design.

The perchlorate absorption efficiency was assessed at different column loading rates to obtain an optimum loading rate by analyzing the perchlorate content of water before and after passage through the column. Our experiments revealed that >99% removal rates of perchlorate are achievable, even at flows as high as 12 BV/ min (300 mL/ min).

For perchlorate desorption from the A530E resin, the perchlorate-laden beads are first transferred from the brass column to a borosilicate glass desorption column (6 mm OD) in the laboratory. The desorption column was constructed at the UCR (University of California- Riverside) glass shop and was constructed with a glass valve in order to assist in controlling eluent flow. A small piece of glass wool was placed near the bottom of the column at the valve joint in order to prevent resin beads from migrating out of the column with the eluent stream. While situated in the desorption column, the ClO₄⁻-laden resin is first rinsed with 3 BV of 4 M hydrochloric acid (HCl) to remove weakly (with respect to perchlorate) sorbed contaminants and to prepare the resin bed for perchlorate desorption. Acidic ferric chloride eluent is then dripped through the resin in the desorption column at a flow rate of ~1 mL/ min using a peristaltic pump. With this configuration, recoveries of perchlorate after 4 BV of eluent have passed through the laden resin were similar to those (e.g., >95%, Table 6, experiment 5 below) observed by Bao and Gu (2004) and Jackson et al. (2010).

Silver oxide addition

The washed and dried Ag₂O is added to the perchlorate-laden eluate in successive steps, stirring with a clean glass rod to break up clumps until a solution pH of 5.5 – 6 is achieved and the chloride is precipitated. Heat generated during this step can be dissipated by keeping the container in ice. The resulting suspension is centrifuged and the clear supernatant (containing dissolved ClO₄⁻) is collected. Perchlorate may partially or completely sorb on and/ or co-precipitate with the iron oxyhydroxides and AgCl pellet and so this is thoroughly washed with Type 1 water and the supernatants combined, repeating these procedures until the perchlorate recovery is complete. Final perchlorate recoveries are determined using IC-ECD.

Prior to freeze drying the perchlorate sample, contamination level are determined in small aliquots of ClO₄⁻ -laden solution and from process blanks using IC-ECD. DOM is analyzed using high temperature catalytic combustion (analytical details given below). Perchlorate solutions containing persistent nuisance contamination (e.g., ≥1‰) can be reprocessed by either A530E (Purolite) resin,

AS16 preparatory chromatography (Dionex) (for nitrate removal), barium addition (for sulfate removal), Ag₂O addition (for chloride removal), or SPE filtration (for DOM removal), as needed.

Freeze drying the purified perchlorate

Solutions containing the purified ClO₄⁻ (as AgClO₄) are added to 100 mL washed rotary evaporation flasks. Rotary evaporation (T=50 °C for ~0.5 h) is used to obtain final solution volumes equal to 2 to 8 mL in order to reduce the subsequent required freeze-drying time. The evaporates are transferred to 10 mL amber borosilicate vials, frozen in liquid N₂, and freeze-dried (Labconco FreeZone12, Labconco Corp., Kansas City, MO, USA) to dryness (time required ~13 h). Lyophilates are resuspended in 2 mL Type I water and filtered through prewashed (Type I water) 0.2 µm nylon filter paper (Cat.#: GNWP02500, Millipore Corp., Billerica, MA, USA) using a plastic syringe (10 mL HSW Norm-Ject, Henke-Sass Wolf, Tuttlingen, Germany).

The AgClO₄ is deliquescent (AgClO₄.xH₂O) and subject to photochemical decomposition resulting in the formation of silver chloride with oxygen loss as O₂ (Pai Vernekar and Maycock, 1968). Thus, it is important to minimize exposure of AgClO₄ to humidity and light.

Experiments - potential sources of perchlorate isotopic interference and perchlorate recoveries

We conducted a series of experiments (detailed below) in order to determine sources of isotopic interference and steps that can be taken to minimize them. We determined the recovery of perchlorate loaded onto the anion-exchange resin, desorbed and purified using the Ag₂O method. Potential isotopic contamination levels were calculated using an assumed 100% recovery of 50 µmol of ClO₄⁻ from the Ag₂O + 'FeCl₃ eluent' mixture with our goal to reduce contamination levels to < 1‰.

experiment 1: To test for any oxygen- and chlorine- contamination introduced by the reagents used in our method, solutions were prepared containing 0.025 L of the acidic ferric chloride (i.e., 1 M FeCl₃/ 4 M HCl) eluent or Type I water, diluted (1:2), and then reacted with a slight stoichiometric excess (~30 g) of washed Ag₂O powder to precipitate the chloride as AgCl. The neutrality (pH 5-6) of the resulting solutions was tested using pH paper. After centrifugation, the clear supernatants were analyzed for anions by liquid chromatography with conductivity detection as described below. In order to determine the effectiveness of Ag₂O washing to remove nitrate, aliquots of Ag₂O required for the experiments were taken at two time steps during the washing of the bulk Ag₂O powder and these are named batches A (t= 992 h; bath change #37) and B (t= 1664 h; bath change #38). The two silver oxide batches, A and B, were oven dried at T=105 °C for 24 h and stored separately.

experiment 2: To test for contamination to and recovery of perchlorate from the rotary evaporation and freeze drying steps, 0.05 L volumes of Type I water blanks and solutions containing ~20 to 50 µmol ClO₄⁻ (as AgClO₄) were prepared using the rotary evaporation and freeze drying procedures detailed above. All glassware was washed according to procedures as described above. Perchlorate recoveries were determined and the process blanks and syringe filter blanks were analyzed for contaminating anions using IC-ECD (described below). Potential isotopic contamination levels were calculated using an assumed 100% recovery of 50 µmol of ClO₄⁻ from the Ag₂O + FeCl₃ mixture.

experiment 3: The DOM contamination associated with the reagents (i.e., Ag₂O powder, 1 M FeCl₃/ 4 M HCl eluent), A530E resin, and from wetted surfaces was measured in duplicate using washed borosilicate glass 50mL - Erlenmeyer flasks consisting of four separate trials: Trial #1) Type 1 water only (control), Trial #2) Type 1 water + Ag₂O, Trial #3) 1 M FeCl₃/ 4 M HCl solution + Ag₂O, and Trial #4) Type 1 water + A530E resin. Each trial solution was heated to four temperatures (T= 22 °C, T = 65 °C, T = 85 °C, and T = 100 °C). The above-ambient temperatures were selected to simulate heat-assisted methods for enhancing ClO₄⁻ desorption.

experiment 4: The effectiveness of two SPE resins (C-18, Supelclean ENVI-18 6 mL tube No. 57064, Supelco, Bellefonte, PA, USA and Silica Gel (precipitated Silicic Acid, A288-500, Fisher Scientific,

Hampton, NH, USA) in column form for post-elution cleanup of reagent-associated DOM was assessed. The solutions from experimental trials (experiment 3 above) that contained measurable DOM were selected for testing the preconditioned (Type 1 water rinsed) SPE resins. The solutions were filtered through the SPE columns and the eluates analyzed for TOC (described below) to reveal SPE effectiveness for DOM removal. In order to determine the usefulness of solvent-based washing procedures for DOM contaminant removal from reagent, we tested solvents in sequence from low polarity to high polarity (i.e., ethyl acetate, acetone, methanol and Type 1 water). Aliquots (40 g each) of washed and oven dried ($T = 105\text{ }^{\circ}\text{C}$) Ag_2O powder were washed successively by ethyl acetate, acetone and methanol (m:v = 1:3) for 8 h each in a glass 50-mL Erlenmeyer flask on a stir plate with a teflon stir bar at ambient temperature ($T = 22\text{ }^{\circ}\text{C}$). Between each solvent washing step, the Ag_2O was rinsed with Type 1 water while situated on 0.2 μm nylon filter paper ((Cat.#: GNWP02500, Millipore Corp., Billerica, MA, USA) using a filtration stand. A subsample of 10 g Ag_2O was oven dried ($T=105\text{ }^{\circ}\text{C}$) then combined with 0.025 L Type 1 water, equilibrated for 2 h, and analyzed for TOC. The three (10 g) Ag_2O aliquots were then dried at $T = 170\text{ }^{\circ}\text{C}$ for 24 h, combined with 0.025 L Type 1 water, equilibrated for 2 h, and each analyzed for TOC. $T = 170\text{ }^{\circ}\text{C}$ was selected to ensure complete removal of any residual solvents that might remain at the $T=105\text{ }^{\circ}\text{C}$ treatment. The thermal decomposition of silver oxide to Ag metal commences at $T\sim 300\text{ }^{\circ}\text{C}$, but decomposition only becomes significant at $T = 490\text{ }^{\circ}\text{C}$ (Weaver and Hoflund, 1994).

experiment 5: Recoveries of perchlorate were assessed after loading (using a 100 mL beaker) known quantities of perchlorate (i.e., $\sim 8\text{ mg ClO}_4^-$ as $\text{AgClO}_4\cdot\text{H}_2\text{O}$; MV Laboratories) onto 10 g (hydrated) A530E anion-exchange resin, desorbing ClO_4^- with 1 M $\text{FeCl}_3 + 4\text{M HCl}$ eluent in a 6mm borosilicate desorption column, and purifying the ClO_4^- using Ag_2O additions, as described above. When packed into the desorption column, the A530E resin bed volume was $\sim 15\text{ mL}$. Four BVs of eluent were used per sample and each BV was stored separately for recovery analysis. The iron oxyhydroxide + AgCl pellet formed was subjected to two wash steps using 30 mL of Type 1 water each with supernatants collected separately for perchlorate recovery determination. Final perchlorate recoveries were determined using IC-ECD (described below).

Thermal decomposition of silver perchlorate and development of isotopic analytical procedures

The thermal decomposition of silver perchlorate was investigated in order to assess stoichiometric yields of O_2 and Cl (as AgCl) for subsequent isotopic analysis. We placed a sample of $\text{AgClO}_4\cdot\text{H}_2\text{O}$ in a Pyrex weighing vial and heated it in a muffle furnace to three temperatures in sequence: $65\text{ }^{\circ}\text{C}$ (4 h soak time), $200\text{ }^{\circ}\text{C}$ and then $600\text{ }^{\circ}\text{C}$, the latter two held for 1 h. After each step, we used thermogravimetric weight loss data to check for stoichiometric losses of perchlorate-associated water of hydration and oxygen. During heating, we placed a small glass funnel on top of the vial to minimize the possibility of spattering losses of the solid while simultaneously allowing the escape of O_2 (or other gaseous products).

Complete proof-of-concept of method (from groundwater to mass spectrometry)

In order to determine the ability of our method to recover and purify natural perchlorate, we sampled groundwater from two southern California sites. Here we coupled perchlorate trapping, desorption, and purification steps into a complete proof-of-concept procedure. The site selection criteria were based on the approach used by Parker et al. (2008) as part of our interests in exploring the origin of natural perchlorate, given here in brief, as follows: 1) avoid known, documented sites of perchlorate use or release, 2) because hypochlorite salts are a potential source of perchlorate contamination (e.g., Dasgupta et al., 2006), we avoided to the extent possible any wells known to have been recently disinfected using hypochlorite or that had an in-line chlorination system. The two sites selected were Granite Mountain (Granite Mountain Desert Research Center, UCNRS, lat = 34.7824 , long = -115.6542) and Sedgewick (Sedgewick Reserve, UCNRS, lat = 34.6949 , long = -120.035).

Analytical Details

The perchlorate concentrations of samples were determined using a Dionex (Sunnyvale, CA, USA) ion chromatograph with electrospray-ionization-mass-spectrometry detection (IC-ESI-MS). The methods used were similar to EPA 331.0 (2005) and EPA 314.0 (1999), with only slight modification. Briefly, chromatographic separation was performed using a DX500 ion chromatograph equipped with an AS50 autosampler and a GP50 gradient pump run in the isocratic mode. The eluent was 45 mM KOH pumped at a flow rate of 0.3 mL/min, and an injection loop of 100 μ L was used. Background conductivity was maintained below 1 μ S/cm with an ASRS 300 (2mm) suppressor at 50 mA in the external water mode using Type 1 water as the regenerant and a CR-ATC trap column. Separation was achieved using an IonPac AS16 (2 \times 250 mm) analytical column equipped with an IonPac AG16 (2 \times 50 mm) guard column. With ESI-MS, flow from the IC was directed into a Finnigan Surveyor MSQ Plus single quadrupole MS (Thermo Electron Corporation, Waltham, MA, USA). The MS was coupled with an Ultimate 3000 auxiliary pump (Dionex), pumping 50/50 acetonitrile/water at a flow rate of 0.3 mL/min. Using a switching valve, all of the IC flow was diverted to waste for the first 9 min of each analysis, after which the IC flow was combined with acetonitrile/water to achieve a total flow rate of 0.6 mL/min to the MS. The retention time of perchlorate was \sim 13 min under these conditions. Flow to the MS was nebulized through an ESI source using ultrahigh purity nitrogen gas at a pressure of 550 kPa. The electrospray capillary was held at 450 $^{\circ}$ C with a needle voltage of 3.5 kV, and the entrance cone was held at a voltage of 70 V. Negative ion monitoring of m/z 99 \pm 0.5, m/z 101 \pm 0.5, and m/z 107 \pm 0.5 (corresponding to $^{35}\text{Cl}^{16}\text{O}_4^-$, $^{37}\text{Cl}^{16}\text{O}_4^-$, and $^{35}\text{Cl}^{18}\text{O}_4^-$, respectively) was utilized with a dwell time of 0.30 s per ion mass. Monitoring at m/z 99 was used for all quantification, and $\text{Cl}^{18}\text{O}_4^-$ (m/z 107) was used as the ISTD at a concentration of 1 μ g/L in all blanks, standards, and samples to correct for any ion suppression. Identification of perchlorate in the unknowns was confirmed by retention times, as well as the m/z 99 to 101 ratio of 3:1 when using ESI-MS. Chromeleon Version 6.80 (Dionex) was used to control the instrumentation and to quantify perchlorate.

The electrical conductivity of all samples was determined using a CDM 83 conductivity meter (Radiometer America, Inc., Westlake, OH, USA) in order to determine dilutions needed for the analytical range of the particular sample analysis. Ion chromatography with an electrical conductivity detector (IC-ECD) was used to determine the concentrations of major and secondary anions (Br⁻, Cl⁻, F⁻, NO₂⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻). The DX-500 ion chromatography system (Dionex, Sunnyvale, CA, USA) consisted of an electrical conductivity detector (DS-3) with an AS19 column (2 \times 250mm), AG19 guard column (2 \times 50 mm), and ASRS 300 suppressor at 50 mA in external water mode with Type 1 water as the regenerant. The system was equipped with an AS50 autosampler and a GP50 gradient pump run in the gradient mode ([KOH]= 10 mM to 30 mM). The eluent was pumped at a flow rate of 0.25 mL/min, and an injection loop of 50 μ L.

Total organic carbon (TOC) was determined by a TOC-V Analyzer (Shimadzu Scientific Instr., Columbia, MD, USA) using high temperature catalytic oxidation. TOC samples for analysis were filtered through prewashed (Type 1 water) 0.2 μ m nylon filter paper (Cat.#: GNWP02500, Millipore Corp., Billerica, MA, USA) using a plastic syringe assembly (10 mL HSW Norm-Ject, Henke-Sass Wolf, Tullerigen, Germany). Unfiltered and filtered controls (Type 1 water) were analyzed for TOC and showed that the filtration procedure did not contribute any DOM. All samples were acidified to pH < 2 with 3 N HCl and were purged with CO₂-free air to remove inorganic C before TOC combustion CO₂ analysis using an infra-red gas analyzer (IRGA).

Dissolved organic matter (DOM) contamination to perchlorate was calculated from the TOC measurements based on estimation of the particular contaminant's DOM- carbon and DOM-oxygen contents. DOM was assumed to have an identical composition to Suwannee River natural organic matter (Cat.#: 1R101N, International Humic Substances Society, St. Paul, MN, USA) with DOM-C = 52.7% and DOM-O = 43.1%. The A530E anion-exchange resin could also contribute DOM via resin degradation (e.g., formation of carbanions at elevated temperatures, Simister et al., 2006). The resin consists of a polystyrene network that is cross-linked with divinylbenzene (DVB), in order to maintain aqueous phase insolubility, with bifunctional (triethylamine-trihexylamine) exchange

groups (Purolite Corp., product literature). The resin oxygen composition was analyzed using an oxygen analyzer (UC-FIRMS Lab, Riverside, CA, USA) and its associated DOM was assumed to be similar (i.e., DOM-O = 7%), with carbon (i.e., DOM-C ~ 92%) representing the balance.

Quality Assurance and Control

For perchlorate IC-ESI-MS analysis, blanks and spiked blanks were made up in synthetic matrix containing the following, in mM: 1.6 HCO₃⁻, 1.0 SO₄²⁻, and 2.8 Cl⁻, all as the sodium salt. Blanks were run every 20th sample and always resulted in a nondetect. Spiked matrix blanks at either 30 or 50 ng/ L perchlorate (bracketing the typical method detection limit; see below and Results) were also run every 20th sample, as well as a spiked matrix blank at 250 ng/ L. Every 10th sample was run in duplicate, and values were only accepted when bracketed by a pair of duplicates that both agreed to within 10%. Perchlorate standards ranged from 0.030 to 10 µg/L and were prepared by dilution of a liquid 1000 mg ClO₄⁻ /L standard solution (SPEX CertiPrep, Metuchen, NJ, USA). Perchlorate spikes were prepared from the same standard. An internal standard (ISTD) was used consisting of Cl¹⁸O₄⁻ (99+% isotopic purity) with m/z values of 107 and 109 in the same 3:1 ratio as the natural abundance of ³⁵Cl and ³⁷Cl (Dionex Corp., Sunnyvale, CA, USA).

Identification of anions in the unknowns was confirmed by retention times using certified calibration standards (Seven Anion Standard, Part # 57590, Dionex). Chromeleon Version 6.80 (Dionex) was used to control the instrumentation and to quantify anion concentrations.

A calibration curve for TOC was performed with standards prepared using potassium hydrogen phthalate.

Analytical Limits

For groundwater chemical analysis, we adopted a widely used method for calculating the method detection limit as described in EPA Method 314.0. Briefly, seven replicate samples are analyzed using either IC-ESI-MS, IC-ECD, or other techniques and the MDL is calculated based on the Student's t-value at the 99% confidence interval. The MDL is given by MDL = $t_{(1-\alpha/2, n-1)} s$ where $t_{(1-\alpha/2, n-1)}$ is 3.14 for six degrees of freedom and s is the standard deviation of the measured concentration in the seven replicates. We adopted a minimum reporting limit (MRL) 3-fold greater than the MDL. Minimum reporting levels (MRL) for IC-ECD are as follows: Cl⁻ = 0.65 µM, NO₃⁻ = 0.64 µM, NO₂⁻ = 1.06 µM, SO₄²⁻ = 0.91 µM, PO₄³⁻ = 0.39 µM, ClO₄⁻ = 0.20 µM. Minimum reporting levels (MRL) for IC-ESI-MS: ClO₄⁻ = 0.98 nM. The MRL for TOC when using the Shimadzu TOC-V was 0.30 mg TOC/ L.

Results and Discussion

Potential isotopic interferences and procedures to minimize their occurrence

Chlorine contamination from the reagents was completely removed by Ag₂O addition (Table 3), as expected by design. Oxygen isotopic interference could result if any residual NO₃⁻ contamination remains in the silver oxide (Ag₂O) powder used (Table 3). Complete nitrate removal from the Ag₂O reagent was attempted using assiduous washing with Type I water of the silver oxide powder. Although, the nitrate concentration of the final rinse waters from the Ag₂O batches A and B was below the IC-ECD detection limit, some nitrate contamination was still evident in the final product water after neutralizing with 1 M FeCl₃/ 4 M HCl solution. The longer wash time and additional bath change for Ag₂O Batch B resulted in a reduced average nitrate contamination level. The replicates for the 'Batch B Ag₂O' + 'FeCl₃ eluent' were similar (±0.6 ‰) and this was the case for the corresponding 'Batch B Ag₂O' + H₂O replicates (±0.4 ‰) as well. Other oxy-anions from reagents were not significant sources of contamination. If sulfate contamination occurs, the method of Silva et al. (2000), whereby a molar excess of barium is added for gravimetric precipitation of sulfate as BaSO₄, may be needed. The levels of oxygen contamination we observed, attributed to residual nitrate in Ag₂O reagent, will likely not be problematic for perchlorate forensics. However, if residual nitrate

becomes problematic, it is possible that the concentrated perchlorate sample could be resorbed onto a small bed volume (BV) of A530E resin, which then has co-sorbed nitrate eluted using 4 M HCl. Desorption of perchlorate with the standard FeCl₃ eluent follows requiring much smaller amounts of Ag₂O corresponding to the smaller BV. Alternatively, the perchlorate could be separated from the nitrate contamination by peak separation using the Dionex IC-ECD system (AS16 column with ASRS 300 suppression) described above with a switching valve to capture the perchlorate peak.

The results from the rotary evaporation and freeze drying of ~20 to 50 μmol of pure perchlorate (silver perchlorate form) are presented in Table 4, and these indicate generally successful recovery of perchlorate (>88.7%), with some introduced background contamination. The <100% recoveries are at least partially due to some losses that occurred during the volume transfer steps associated with freeze drying and rotary evaporation. Fortunately, such losses will not result in any isotope fractionation. The chlorine contamination observed (4.04 ‰) in the second process blank might be due to some residual chlorine that remained from previously HCl acid-washed glass surfaces of the rotary evaporation condenser's interior that had not been rinsed sufficiently and thus entered the evaporation flask. The third process blank was produced after carefully washing (1 M acetic acid bath) and rinsing (Type I water) the condenser glass interior a second time. This was effective in reducing chloride- and oxygen- contamination. The glassware appears to be the only potential source of chlorine contamination in our method since this glassware comes into contact with the perchlorate-laden solution *after* the silver chloride precipitation step. Fortunately, this source of contamination can be easily washed away from the glass surfaces, but care needs to be taken.

Table 3. (Experiment 1). Silver oxide and FeCl₃ reagents: contributions to oxygen- and chlorine-contamination levels.

Reagents Added	Ag ₂ O batch	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻	Potential Isotopic Contamination per 10 g Ag ₂ O*	
						Cl	O
----- μmol/ 10 g Ag ₂ O -----						----- ‰ -----	
Ag ₂ O + FeCl ₃ solution**	A	0.008	0.021	0.763	0.044	0.17	12.25
Ag ₂ O + FeCl ₃ solution	B	ND	0.018	0.048	ND	ND	1.07
Ag ₂ O + FeCl ₃ solution	B	ND	ND	0.016	0.025	ND	0.49
Ag ₂ O + H ₂ O	A	ND	ND	0.671	0.074	ND	10.76
Ag ₂ O + H ₂ O	B	ND	ND	0.124	ND	ND	1.85
Ag ₂ O + H ₂ O	B	ND	ND	0.044	0.079	ND	1.45
Process blank	NA	ND	ND	ND	ND	ND	ND
Process blank	NA	ND	ND	ND	ND	ND	ND

* assuming 50 μmol ClO₄⁻ recovered

** 1 M FeCl₃ + 4 M HCl

Table 4. (Experiment 2). Rotary-evaporation and freeze drying contributions to oxygen- and chlorine- contamination levels (assuming 50 $\mu\text{mol ClO}_4^-$ recovered) and associated perchlorate recoveries.

Description	ClO_4^- added μmol	ClO_4^- recovered μmol	ClO_4^- % Recovery	Cl^- ----- μmol -----	NO_3^- ----- μmol -----	SO_4^{2-} ----- μmol -----	Potential Isotopic Contamination	
							Cl	O
							-----	%o -----
<i>Contamination levels</i>								
Process blank-1	0	ND	NA	0.031	0.116	0.007	0.63	1.86
Process blank-2	0	ND	NA	0.202	0.070	0.003	4.04	1.10
Process blank-3	0	ND	NA	0.052	0.019	0.005	1.03	0.40
filter blank-1	0	ND	NA	0.003	ND	ND	0.06	ND
filter blank-2	0	ND	NA	0.001	ND	ND	0.02	ND
<i>Perchlorate(as AgClO₄) recoveries</i>								
recovery - 1	52.5	50.6	96.3					
recovery - 3*	22.6	20.1	88.7					
recovery - 4	42.4	38.3	90.3					
recovery - 5	52.5	47.9	91.2					
recovery - 6	57.1	57.7	101.1					

* Trial 2 was lost

The amount of DOM contamination from the reagent Ag_2O was significant (see Table 5) contributing 6.23 to 8.26 ‰ oxygen to a hypothetical 50 μmol of perchlorate recovered for isotope analysis. The trial combining acidic ferric chloride solution and Ag_2O (Trial #3) resulted in a reduced (~60% reduction), although still substantial, level of oxygen contamination. This reduction in DOM might have resulted when at neutral pH, ferric salts precipitate as amorphous hydrated oxide or oxyhydroxides (Murphy, 1976) that have surface properties, which could adsorb at least a portion of the contaminating DOM (Kaiser, 2003). This mechanism of DOM removal, if present, is not effective enough to obtain the high purity ClO_4^- desired. Experiment 4 (described below) details a method for removing this source of DOM contamination. The effect of temperature on resin degradation and concomitant release of DOM is substantial (trials # 4b-4c, Table 5) and so any efforts to enhance ClO_4^- desorption from the A530E resin ClO_4^- elution using elevated temperatures are best avoided. Levels of DOM oxygen contamination (<0.5 ‰) resulting from the A530E resin with ClO_4^- elution at ambient temperatures (i.e., trial# 4a, T = 22 °C, Table 5) are likely not a concern for perchlorate isotopic analysis.

The SPE resins (i.e., C-18 and silica gel) were not effective in reducing DOM contamination from reagents and from the heated A530E resin in order to attain the high purity AgClO_4 desired (data not shown). The A530E resin-derived DOM was more effectively removed than Ag_2O -associated DOM (~75% removal versus ~0% removal). The C-18 SPE resin was more effective perhaps reflecting the non-polar nature of A530E resin degradation products formed during A530E resin heating. The mixed success of SPE resins is indicative of the heterogeneous nature of DOM from contamination sources and the need for, perhaps, multiple SPE types for their removal. For example, Michalski (2010), in preparing high purity nitrate salts for isotopic analysis, utilized three different SPE materials having absorption properties reflecting the type of intra molecular forces typical of DOM. In addition to C-18 and silica gel, he used water insoluble, cross linked poly-vinylpyrrolidone, which is known to bond with the hydroxyl groups of polyphenols, polysaccharides and humic substances, thus

removing them from solution. If DOM contamination is a concern, these methodologies for DOM removal could be employed. Alternatively, hydrogen peroxide has been used by some researchers, but their methods were not detailed (Jackson et al., 2010). Since perchlorate desorption from the A530E resin is effective at ambient temperatures (e.g., Jackson et al., 2010) and since a method for reducing DOM contamination originating from Ag₂O was developed (see experiment 4), SPE resins are not needed.

Table 5. (Experiment 3). Sources and magnitudes of DOM-associated oxygen contamination to AgClO₄.

Trial #	DOM Source	mass of added solids		solution volume	TOC	DOM – Oxygen	Potential ²
		g Ag ₂ O	g resin				O Isotopic Contamination of ClO ₄ ⁻
	<i>Reagents</i>			L	Mg/ L	μmol/10 g (wet) Ag ₂ O	‰
1	water (control)	0	0	0.05	ND	ND	ND
1 (rep)	water (control)	0	0	0.05	ND	ND	ND
2	Ag ₂ O + water	10	0	0.05	0.49	1.25	6.23
2 (rep)	Ag ₂ O + water	10	0	0.05	0.65	1.66	8.26
3	Ag ₂ O + FeCl ₃ eluent	30	0	0.05	0.75	0.64	3.18
3 (rep)	Ag ₂ O + FeCl ₃ eluent	25	0	0.05	0.55	0.56	2.77
	<i>Resin</i>					DOM-O μmol/20 g (wet) resin	
4a	water + resin, T = 22 °C	0	5	0.025	0.39	0.05	0.23
4a (rep)	water + resin, T = 22 °C	0	5	0.025	0.54	0.06	0.32
4b	water + resin, T = 65 °C	0	5	0.025	10.69	5.08	25.29
4b (rep)	water + resin, T = 65 °C	0	5	0.025	9.54	4.54	22.56
4c	water + resin, T = 85 °C	0	5	0.025	12.60	5.99	29.81
4c (rep)	water + resin, T = 85 °C	0	5	0.025	11.47	5.46	27.14
4d	water + resin, T = 100 °C	0	5	0.025	14.21	6.76	33.62
4d (rep)	water + resin, T = 100 °C	0	5	0.025	41.53	19.75	98.26

The Ag₂O powder was washed sequentially with solvents of increasing polarity in an effort to remove the known DOM contamination (Table 5). None of the solvents were successful in removing this contamination, but instead heating the Ag₂O appears to be a significant factor in removing DOM (Table 6). It is apparent that the Ag₂O heating to T = 170 °C (24 h) not only removed residual solvent, but also the persistent DOM contamination associated with Ag₂O. We have not identified the origin of DOM associated with Ag₂O, but we strongly recommend adopting Ag₂O heating to eliminate its occurrence when using it to form high purity silver perchlorate for isotopic analysis.

Table 6. (Experiment 4). The effectiveness of solvent washing and heating of Ag₂O + solvent for removal of DOM-associated oxygen contamination of AgClO₄.

Ag ₂ O Solvent Washes	mass of solids	water volume	TOC	DOM - Oxygen	Potential O Isotopic Contamination of ClO ₄ ⁻
	g Ag ₂ O	L	mg/L	μmol/ 10 g (wet) Ag ₂ O	‰
<i>'Ag₂O + solvent' drying temperature, T = 105 °C, time = 24 h.</i>					
Water wash	10	0.050	0.57	1.46	7.25
Ethyl acetate wash	10	0.050	110.0	140.57	699.3
Ethyl acetate + Acetone wash	10	0.050	0.91	0.60	3.00
Ethyl acetate + Acetone + Methanol wash	10	0.050	1.77	0.37	1.83
<i>'Ag₂O + solvent' drying temperature, T = 170 °C, time = 24 h.</i>					
Water wash	10	0.050	ND	ND	ND
Ethyl acetate wash	10	0.050	ND	ND	ND
Ethyl acetate + Acetone wash	10	0.050	ND	ND	ND
Ethyl acetate + Acetone + Methanol wash	10	0.050	ND	ND	ND

When using Ag₂O additions for purification, perchlorate recoveries (>95%; Table 7) after 4 BV of 1 M FeCl₃ + 4 M HCl eluent have passed through the laden A530E resin were comparable to those reported by Bao and Gu (2004) and Jackson et al. (2010) using gravimetric precipitation recovery. Successful recovery of perchlorate required washing the iron oxyhydroxide + AgCl pellet that forms, after Ag₂O addition, at least two times using Type 1 water.

Table 7. (Experiment 5). Recoveries of ClO₄⁻ (as AgClO₄) after A530E sorption, FeCl₃ eluent desorption, and purification using Ag₂O additions. Pellet wash steps were to remove perchlorate from the oxyhydroxide/ AgCl precipitate that forms after Ag₂O addition.

ID	BV	Desorption %ClO ₄ ⁻ recovered	Pellet wash 1 %ClO ₄ ⁻ recovered	Pellet wash 2 %ClO ₄ ⁻ recovered	Sub Total %ClO ₄ ⁻ recovered
LLHARD2	1	17.5	19.9	14.6	52.0
LLHARD2	2	8.2	9.0	4.4	21.7
LLHARD2	3	5.9	5.6	2.8	14.2
LLHARD2	4	2.8	5.3	1.3	9.4
				TOTAL %ClO ₄ ⁻	97.2
LLHARD3	1	15.9	11.0	4.1	31.0
LLHARD3	2	21.4	16.4	4.6	42.4
LLHARD3	3	8.6	8.8	3.2	20.6
LLHARD3	4	0.1	2.2	0.7	2.9
				TOTAL %ClO ₄ ⁻	96.9

Thermal decomposition and dehydration of silver perchlorate and development of isotopic analytical procedures

From thermogravimetry, heating silver perchlorate monohydrate and weight loss data was consistent with loss of monohydrate at 65 to 200 °C and decomposition of perchlorate with loss of 2 O₂ at 500 °C (Table 7). The dehydration step occurs in at least two stages (Table 7) and this is not unprecedented for perchlorate salts (e.g., NaClO₄.H₂O; Devlin and Herley, 1987). The weight loss due to dehydration did not occur until the temperature exceeded 150 °C. The salt changed color (from white to tannish) at 200 °C, in accord with the literature description of the rhombic-cubic transition (Solymosi, 1977).

The course of decomposition of perchlorate salts is complicated by the simultaneous occurring phase changes resulting from a lowering of the melting point by the accumulation of reaction products, e.g., chloride and chlorate salts, and a subsequent freezing of the melt as the material becomes predominantly the chloride salt (Solymosi, 1977). Silver chloride, the product has a melting point of 455 °C and a boiling point of 1502 °C (CRC Handbook Chem. And Phys., 2008-09); otherwise it should be stable over the temperature range of interest. Silver perchlorate decomposition might be more straightforward than decomposition of alkaline metal perchlorates. Decomposition of the latter perchlorates are known to be complex, with a chlorate intermediate present, which is not found as a decomposition intermediate for silver perchlorate (Solymosi, 1977). The standard state enthalpy of formation of the silver perchlorate (e.g., $\Delta H^0 = -7.75$ kcal/mol) is more than an order of magnitude lower than that of the other perchlorate salts (e.g., CsClO₄, $\Delta H^0 = -105.86$ kcal/mol). This value, representing a minimum of the activation energy needed for decomposition, indicates that the silver perchlorate might decompose more readily and indeed the only described decomposition reaction for the silver perchlorate is $\text{AgClO}_4 \rightarrow \text{AgCl (s)} + 2\text{O}_2 \text{ (g)}$ (Solymosi, 1977).

Table 7. Expected and observed sequential %weight loss from AgClO₄ H₂O (MV Laboratories) during heating in a muffle furnace.

	Temperature, °C		
	65	200	500
Decomposition expected	Loss of 1 H ₂ O		Loss of 2 O ₂
Expected, % wgt. loss	8	0	36.4
Observed, % wgt. loss	3.7	7.5	38.6

In addition to the gravimetric tests for thermal decomposition of silver perchlorate, we performed a series of tests for the temperature and time needed for complete decomposition. In all cases, 25-50mg silver perchlorate (AgClO₄) was added to a pyrex tube. This tube was attached to a peristaltic pump via a short piece of rubber tubing. Samples were then placed in a muffle furnace with the top of the tube extending out of the top of the furnace by several inches. The furnace was programmed to heat up to a setting below the target temperature, and then to ramp and hold at the target temperature. Evolved gasses were passed over a semi-permeable membrane that was attached to a dry ice/acetone water trap and dried gasses that passed through the membrane were measured by a residual gas analyzer.

Tests confirm that oxygen is the primary gas evolved, and that the decomposition speed is a function of temperature. The lowest maximum temperature assessed was 400° C, and the reaction reached a maximum oxygen signal 9 hours after reaching the set point. At 445° C this maximum was reached after 30-60 minutes. These results suggest that whereas the literature values for silver perchlorate

decomposition is in the range of 480° C, the reaction will occur at lower temperatures. This fact could be exploited if contaminating species do not decompose at temperatures between 400 and 450° C, or perhaps even lower temps than this if sufficient time (e.g., (24 hours? 48 hours?)) is allowed for complete AgClO_4 decomposition inside evacuated tubes. Any low temperature decomposition will complicate efforts to pre-clean a silver perchlorate sample via heating. The issue of fractionation is of primary concern in this context, as a complete reaction would be necessary to enable measurement of the analytical variable of interest, to precision adequate for isotope forensics. It might be feasible to design a hybrid RGA/open tube sample preparation method, wherein the reaction is monitored and oxygen is collected for isotope ratio measurement in a specialized cryotrap. In this case, contaminants could be removed while assuring that none of the perchlorate-derived oxygen is lost.

There was limited and somewhat variable detections of gaseous species other than oxygen, in some cases coincident with the oxygen signal and in some cases preceding it. In all cases, these non-oxygen signals were significantly lower than the oxygen signal (Figure 1). This result is suggestive that the RGA method developed may be appropriate to interrogate perchlorate samples purified from environmental sources: contaminants that are evolved during the heating/decomposition of silver perchlorate should be apparent. It should be noted that the membrane introduction mass spectrometry does not lend itself to simple quantitation of gasses; this method is more appropriate for relative comparisons of an analyte (oxygen) versus a contaminant (e.g., nitrate or organic-derived oxygen).

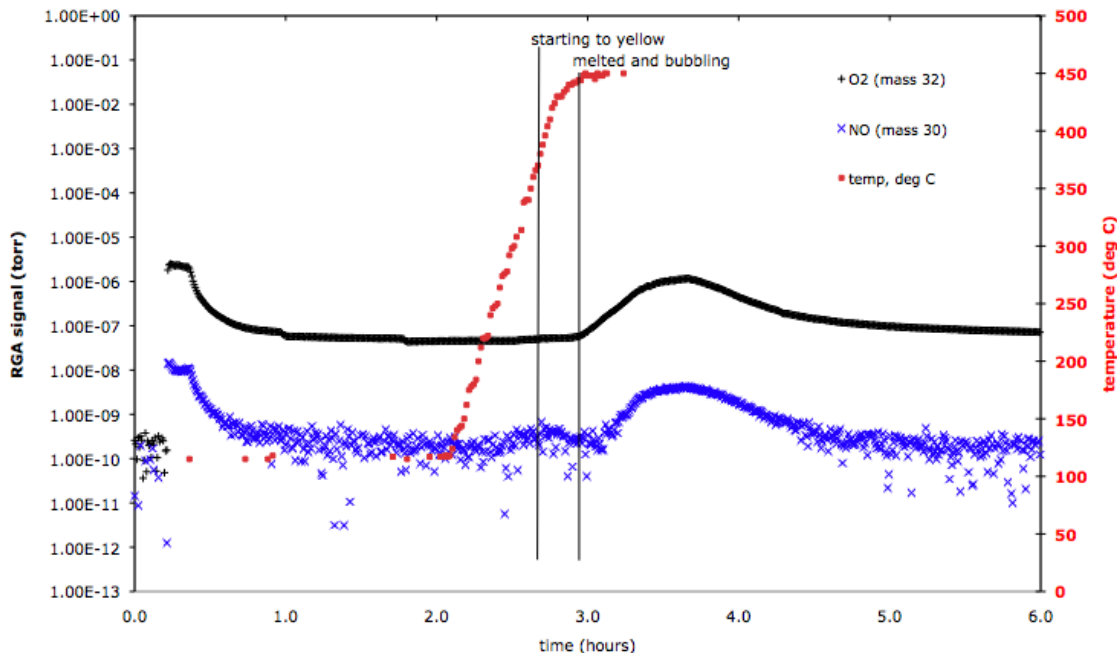


Figure 1: Heating test, showing trace for O₂ and NO. Note that when the silver perchlorate began to yellow there was a small increase in the mass 30 peak. This phenomenon is reasonably consistent, and is also seen in other mass peaks (such as mass 44, CO₂). I attribute this to early stages of melting, or perhaps a crystal rearrangement that releases trapped gasses. Note that there is limited evolution of oxygen during the early phase of heating, and when the temperature reaches ~450° C the crystals melted and the evolution of oxygen accelerated.

Conclusions

Procedures developed appear to be amenable to enable high precision stable isotopic analyses, as

well as lower precision AMS analyses of ^{36}Cl . Immediate work is in analyzing perchlorate isotope standards and developing full analytical accuracy and uncertainty expectations. Field samples have also been collected, and will be analyzed when final qa/qc samples are deemed acceptable.

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