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AIR FORCE MATERIEL COMMAND LAW OFFICE

Directorate of Environmental Law

AFMC LO/JAV

TELEFAX TRANSMISSION COVERSHEET

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PHONE:	
FAX:	415-744-2180 AND 702-798-3146
FROM:	**Major Dan Rogers**
ORGANIZATION:	AFMC LO/JAV
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DATE:	
# OF PAGES:	

COMMENTS: Our review of the California perchlorate protocol

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12/15/97

MEMORANDUM FOR **Maj Dan Rogers, USAF**
AFMC LO/JAV
Building 15, Room 130A
1864 - 4th St
Wright Patterson AFB, OH 45433

FROM: OL AL HSC/OET
2856 G Street
Wright-Patterson AFB OH 45433-7400

SUBJECT: ***Review of California Department of Health Services' Method for Perchlorate Analysis***

1. Per your request, we have reviewed California Department of Health Services' (DHS') standard operating procedure entitled "Method for Determination of Perchlorate by Ion Chromatography (IC), Method Revision 0", dated 3 June 1997. In addition to the documents provided by Dr. David P. Spath of DHS, supplemental information, including the chromatograms, method detection limit (MDL) data and quality assurance/quality control figures, were provided by Mr. Howard Okamoto. Our review and comments concerning the method, chromatography, method detection limit (MDL), practical quantitation limit (PQL) and its applicability to non-laboratory reagent grade water are as follows.

2. Compared to the typical injection volume of 35~50 µL, DHS' method called for an injection volume of 740 µL. For IC methods using conductivity detectors, two problems are usually associated with a large injection volume: peak broadening due to mass overload and base-line perturbation due to the amount of dissolved solids. DHS attempted to compensate peak broadening by using *p*-cyanophenol, an organic modifier, to sharpen the perchlorate peak. The use of organic solvent modifiers to resolve polarizable anions, such as perchlorate, by reducing the affinity of the polarizable anion to the hydrophobic column resin has been demonstrated elsewhere. Some of the organic modifiers, such as hydrogen cyanurate ions and acetonitrile, offered great perchlorate peak symmetry, while others such as phthalate could cause a delayed retention of perchlorate on the IC column and the degradation of the perchlorate peak. With *p*-cyanophenol, retention delay of the perchlorate peak per DHS' method was not observed. However, due to the large aliquot of sample and *p*-cyanophenol , all of the chromatograms available to us showed noisy baseline and systematic baseline drift. The chromatography of the perchlorate is marginally acceptable. The chromatograms of 1, 2.5 and 4 ppb (µg/L) perchlorate (Attachments 1-3) showed peak degradation and tailing. We could not identify the perchlorate

peak in the chromatogram of 1 ppb perchlorate (Attachment 1). As far as the effect of base-line perturbation which showed up right after the water dip, DHS maintained that the perchlorate peak is in the region where the baseline is stable and demonstrated that the matrix spike recovery is within the acceptable range.

3. Per guidelines and procedures set forth in Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B, we have carefully evaluated the raw MDL data (Exhibit 4) for three levels of spiked concentration (1, 2.5 and 4 ppb) generated on 14-20 March 1997. Respectively, our calculated MDLs at 1, 2.5 and 4 ppb perchlorate spike concentrations were 0.9, 0.9 and 0.8 ppb, rather than 0.6, 0.8 and 0.7 ppb as reported by DHS. The calculated percent coefficients of variation (%CV) for the 1, 2.5 and 4 ppb data were 48%, 15% and 6%, respectively. The large %CV for the 1 and 2.5 ppb data is unacceptable. Hence, the 1 ppb data was not used in our pooled MDL calculation. Our calculated pooled MDL with the 2.5 and 4 ppb data is 1 ppb. Theoretically, we should be able to qualitatively and quantitatively identify the peak at 1 ppb with 99% confidence but we could not (see Attachment 1). This discrepancy is attributed to the unusually noisy base-line and marginally acceptable chromatography. In lieu of these problems, we recommend DHS to generate a CV profile by plotting the %CV versus the concentration and determining the minimum detectable concentration at 10 %CV. Based on this method and using the data provided, the minimum detectable concentration at 10 %CV is 3 ppb. The MDL calculated based on EPA's guidelines and the CV profile method should be approximately the same.

4. We're not sure how DHS was able to obtain MDL data at 1 or even at 2.5 ppb with the chromatograms presented to us. It is uncertain if the signal to noise ratio for the 1 or 2.5 ppb data is 3 or better. The variability of perchlorate retention time for the 1 ppb data is an unacceptable 38 %CV. DHS may have manually integrated the perchlorate peak to get the raw data. Manual integration at low concentrations is acceptable if DHS applied the same integration rules to all of the data points. Per aforementioned USEPA guidelines, MDL determination is appropriate and acceptable if and only if all of the data are obtained through the same process. Regardless of the analysts' experience in chromatography, we strongly discourage manual integration for it adds systematic bias to the results. Hence, the calculated MDL is invalid if the data were obtained by both manual and automated integration. Assuming the MDL calculated in accordance with EPA's guideline is valid, the method PQL set at between 5 to 10 times the MDL is 5 ppb to 10 ppb. The method PQL based on the more appropriate CV profile method is between 15 to 30 ppb.

5. We feel that the method is acceptable and applicable to non-potable water as long as the baseline perturbation and tailing, due to the amount of dissolved solids, do not interfere with the

perchlorate peak shape and providing the sample fortification procedures, per method, is carefully followed.

6. Please let me know if you have any questions. Thanks.

DAVID T. TSUI, USAF
Analytical Chemistry Group Administrator
Toxicology Division
Occupational and Environmental
Health Directorate

References

1. State of California Department of Health Services Sanitation and Radiation Laboratories Branch's CLO4-SOP, Rev. No.: 0, 7 May 1997.

2. Aerojet Analytical Laboratory's SOP No. AAL-EA-034 and method validation package, August 1996.

3. Tsuid, D.; Narayanan, L. AL/OET SOP AC-96-036, August 96.

4. Fitchett, A. Dionex Application Record No. 269, Dionex Chromatography Database 4.2.0., Dionex Corp., Sunnyvale, CA.

5. Maurino, V.; Minero, C. *Anal. Chem.* 1997, *69*, 3333-3338.

6. Jandik, P.; Li, J. B.; Jones, W. R.; Gjerde, D. T. *Chromatographia.* 1990, *30*, 509-17.

7. Biesaga, M.; Kwiatkowski, M.; Trojanowicz, M. *J. Chromatogr. A.* 1997, *777*, 375-381.

8. Rendl, J; Seybold, S, Borner, W. *Clin. Chem.* 1994, *40*, 908-913.

Data Reprocessed On 12/09/1997 16:53:58

Sample Name: 1.0 ppb	Date: 03/14/1997 11:11:26
Data File : C:\DX\DATA\CLO4\MDLSTUDY\CLO40001.D24	
Method : C:\DX\METHOD\CLO4.met	
ACI Address: 1 System: 1 Inject#: 24	Detector:CDM-2
Analyst : Rishi Column: AS-5-9488+AG 5 -7515(10-32)	

Calibration	Volume	Dilution	Points	Rate	Start	Stop	Area	Reject
External	1	1	3000	5Hz	0.00	10.00	10000	

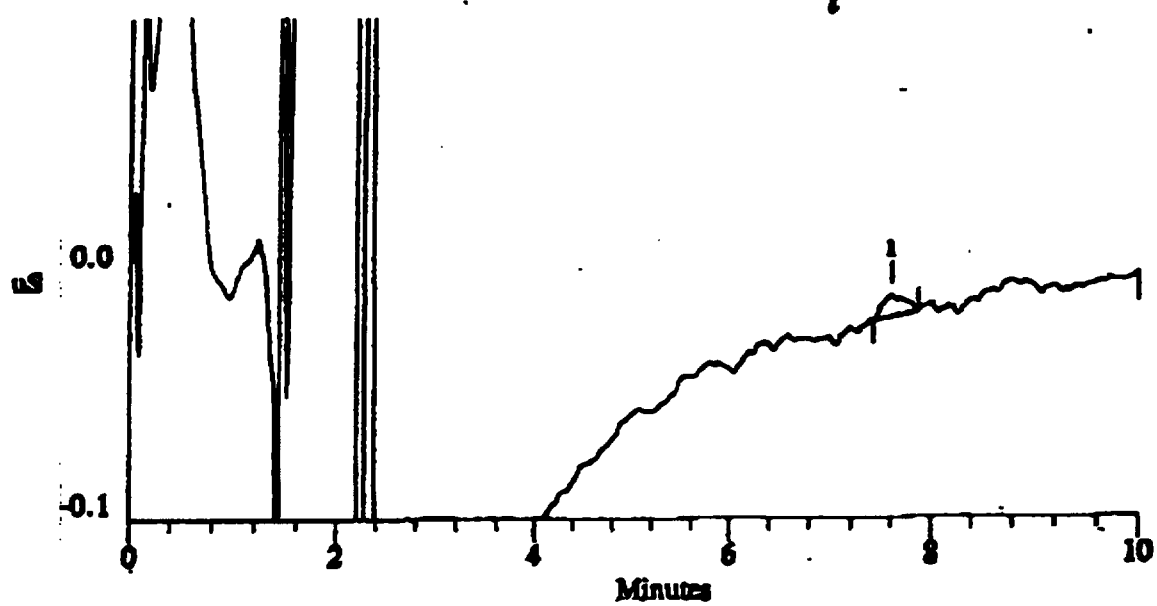
********** Component Report: All Components **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
1	7.60	Perchlorate	0.824	9050	129634	1	2.01
		Totals	0.824	9050	129634		

********** Peak Report: Unknown Peaks **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
		Totals	0.000	0	0		

File: CLO40001.D24 Sample: 1.0 ppb ClO_4^-



Attch 1

Data Reprocessed On 12/09/1997 16:55:37

Sample Name: 2.5 ppb Date: 03/14/1997 11:24:48
Data File : C:\DX\DATA\CLO4\MDLSTUDY\CLO40001.D25
Method : C:\DX\METHOD\CLO4.met
ACI Address: 1 System: 1 Inject#: 25 Detector:CDM-2
Analyst : Rishi Column: AS-5-9488+AG 5 -7515(10-32)

Calibration	Volume	Dilution	Points	Rate	Start	Stop	Area	Reject
External	1	1	3000	5Hz	0.00	10.00	10000	

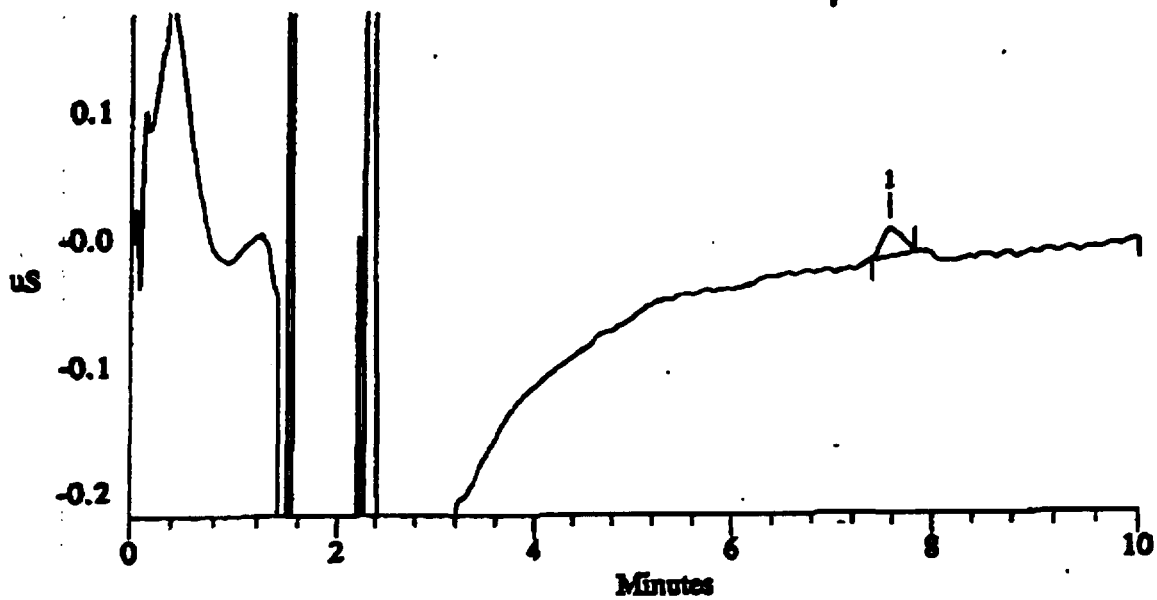
********** Component Report: All Components **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
1	7.56	Perchlorate	2.128	22422	307426	1	2.86
		Totals	2.128	22422	307426		

********** Peak Report: Unknown Peaks **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
		Totals	0.000	0	0		

File: CLO40001.D25 Sample: 2.5 ppb ClO_4^-



Attach 2

2

Data Reprocessed On 12/09/1997 16:56:09

Sample Name: Parr- 4 ppb Clo4 Date: 03/14/1997 11:38:12
Data File : C:\DX\DATA\CLO4\MDLSTUDY\CLO40001.D26
Method : C:\DX\METHOD\CLO4.met
ACI Address: 1 System: 1 Inject#: 26 Detector:CDM-2
Analyst : Rishi Column: AS-5-9488+AG 5 -7515(10-32)

Calibration	Volume	Dilution	Points	Rate	Start	Stop	Area	Reject
External	1	1	3000	5Hz	0.00	10.00		10000

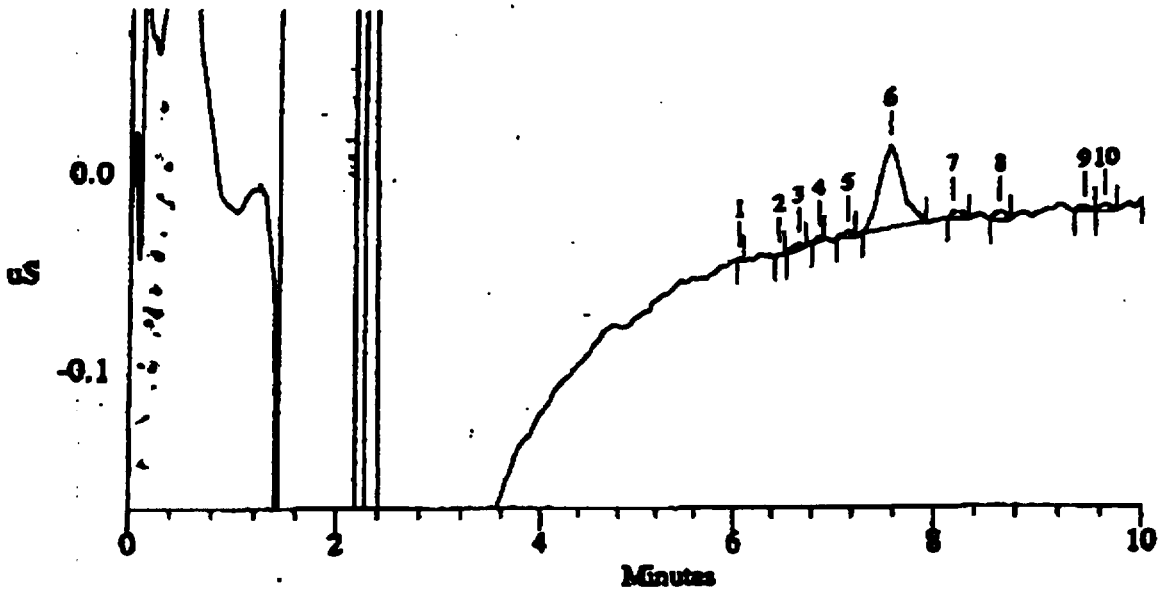
********** Component Report: All Components **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
5	7.15	Perchlorate	0.295	3624	19796	1	-2.77
		Totals	0.295	3624	19796		

********** Peak Report: Unknown Peaks **********

Pk. Num	Ret Time	Component Name	Concentration ppb	Height	Area	Bl. Code	%Delta
3	6.65		0.000	3383	24486	1	
4	6.86		0.000	2901	11528	1	
6	7.56		0.000	41792	630928	1	
7	8.17		0.000	3502	28784	1	
8	8.63		0.000	4305	31320	1	
9	9.43		0.000	2550	18510	1	
10	9.63		0.000	2959	23424	1	
		Totals	0.000	61393	768980		

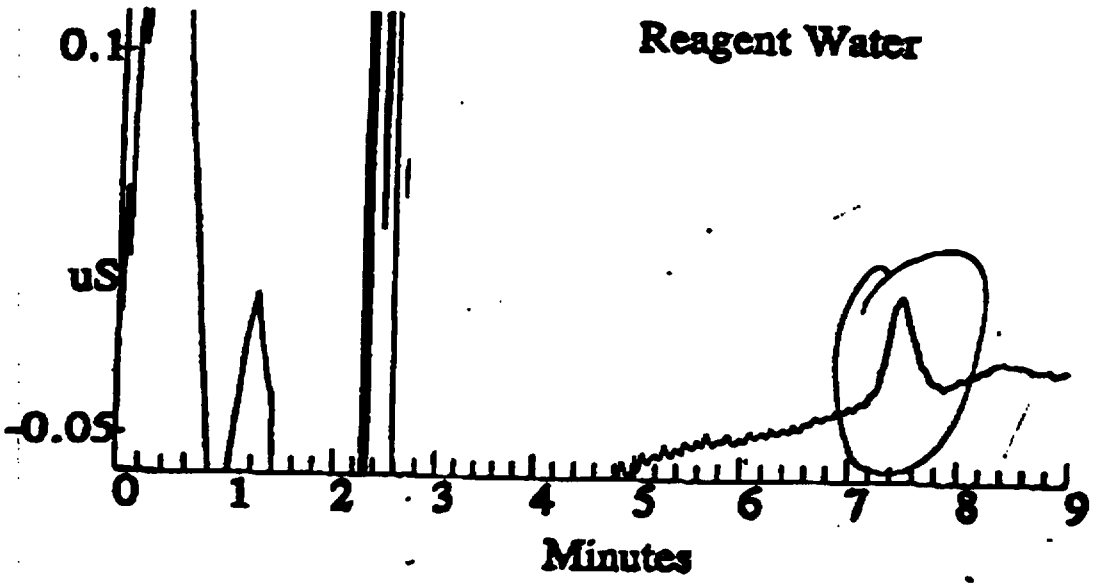
File: CLO40001.D26 Sample: Parr- 4 ppb Clo4

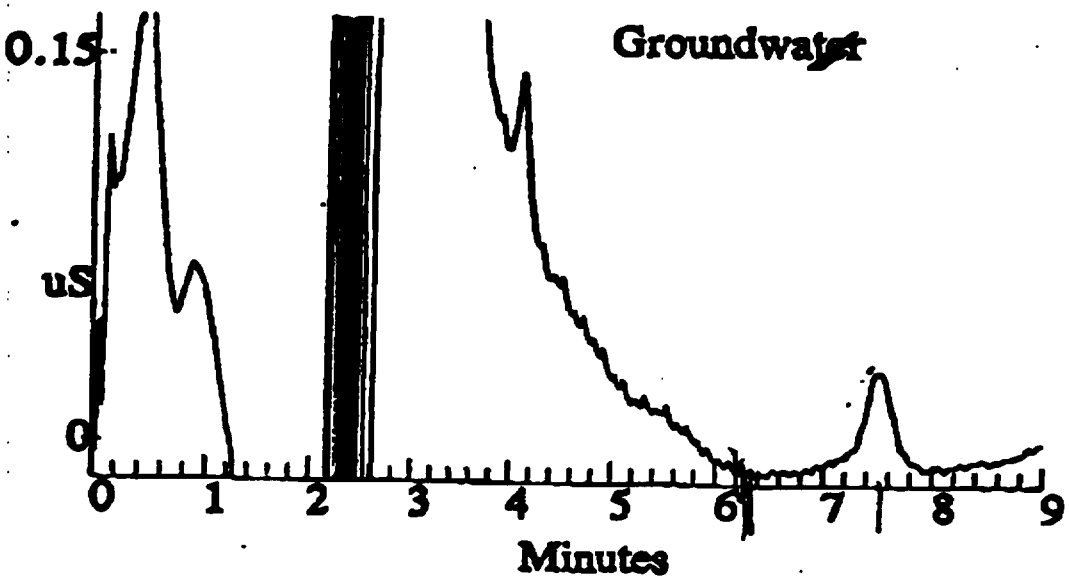


Attack 3

3

FIGURE 1. CHROMATOGRAMS OF 4 µg/L PERCHLORATE ADDED TO REAGENT WATER AND TO A GROUNDWATER SAMPLE





Attach 4

DEPARTMENT OF THE AIR FORCE
AIR FORCE RESEARCH LABORATORY (AFMC)

MEMORANDUM FOR AFMC LO/JAV

ATTENTION: MAJ ROGERS

FROM: AFRL/MLQE

139 Barnes Drive, Suite 2

Tyndall AFB, FL 32403-5323

SUBJECT: Evaluation of California Ion Chromatography Method

1. As requested by your office we have conducted a review of the California standard operating procedure for determination of Perchlorate using Ion Chromatography. The protocol is well written and demonstrated for the matrices cited. The QA/QC measures taken are very thorough and should eliminate most variations and be valid for perchlorate analysis in drinking water, groundwater, and reagent waters.

2. If you have any further questions on this matter please contact Mr. Jim Hurley at DSN 523-6243 or Stan Rising at DSN 523-6203.

Allan M. Weiner, Lt Col, USAF

Chief, Environmental Technology Branch

Post-it® Fax Note 7671	Date	# of pages ▶ 3
To MAJ (P) Van Rogers	From Stan Rising	
Co/Dept. LO/JAV	Co MLQ	
Phone #	Phone # 525-6203	
Fax # 787-0537	Fax #	

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Evaluation of Determination of Perchlorate by Ion Chromatography method *published by the State of California Department of Health Services*

1. Scope and Application

1.2.1 Drinking water, groundwater and reagent waters: This method has been found to perform adequately on water samples with conductivities up to 1000 umhos/cm. Water samples with conductivities > 1000 umhos/cm have not been tested.

- Display chromatograms and corresponding QA/QC data to demonstrate applicability to samples with varying conductivities. No specific data is shown to demonstrate this statement.

7. Reagents and Standards

7.4.3 The analyst should be aware of the purity of the potassium perchlorate used to prepare the stock standard. A weight correction must be made when the solid material is less than 99% pure.

- Suggest that the 99% pure figure be changed to state a 99.5% purity. This will result in more accurate calibration standards.

12. Data Analysis and Calculations

12.1 When quantitating sample concentrations < 100 ug/L, best results are obtained by using peak height calibration mode and a calibration range of 2.5 to 100 ug/L. For sample concentrations > 100 ug/L, the full calibration range should be used.

- Show demonstrated results that for perchlorate concentrations of < 100 ug/L, peak height is the most accurate and reproducible calibration and quantitation method. Is area calibration mode used for samples with perchlorate concentrations of > 100 ug/L? This is not clear.

12.6 Report the perchlorate results in ug/L.

- Perchlorate results should be reported with corresponding error ranges. All QA/QC data should be reported for each run directly corresponding to the perchlorate sample set results.

14. Method Performance

14.2 Tables 2 and 3 give the single laboratory accuracy and precision for perchlorate in reagent water and in groundwater for the listed conditions.

14.3 Table 4 gives the single laboratory precision for replicate analyses of perchlorate in groundwater samples.

- These tables appear to demonstrate both single laboratory and single operator/analyst accuracy and precision data. A statement should be made concerning operator variations and the error associated with such variation.

This method is very well written and demonstrated for the matrices cited. The QA/QC measures taken are very thorough and should eliminate most variation. Careful consideration should be taken when applying this method to water samples with high conductivities and varying sample matrices. This method appears to be valid for perchlorate analysis in drinking water, groundwater, and reagent waters.