State Water Resources Control Board

Division of Drinking Water and Environmental Laboratory Accreditation Program

Allowance Granted for Drinking Water Methods

August 10, 2022

Christine Sotelo
Christine Sotelo
Program Manager, ELAP

Karen Nishimoto
Karen Nishimoto
Quality Assurance Manager, DDW

SUBJECT: Use of EPA Methods 524.3 and 524.4 without Refrigerated Autosamplers

The United States Environmental Protection Agency (US EPA) Technical Support Center (TSC) distributed a technical memorandum to California identifying a method allowance for US EPA 524.3 and 524.4. The memo alleviates the requirement found in US EPA methods 524.3 and 524.4 for the laboratory to utilize a refrigerated autosampler. During the development of these methods, the US EPA required the refrigerated autosampler to reduce degradation of analytes not federally regulated, but within the scope of the method. Importantly, those degradation concerns were not observed with any of the VOC analytes that are currently federally regulated under the US EPA's drinking water program. ELAP offers accreditation for some analytes identified in the US EPA memo as affected by thermal degradation. Laboratories seeking to obtain accreditation for these impacted analytes by these methods must have a procedure to minimize or eliminate the impact thermal degradation would have on sample results.

Laboratories who wish to use these methods without a refrigerated autosampler must reference the allowance granted by the US EPA in their Standard Operating Procedure and retain the US EPA TSC memo in their system of record. Laboratories can obtain copies by downloading them from ELAP's website, or by requesting a copy with an email to elapca_technical@waterboards.ca.gov with the header: "US EPA 524 Memo Request".

Alternative Gasses Used for Methods

Using Nitrogen as a Purge Gas in EPA Method 524.4

Currently, only US EPA method 524.4 allows for the use of nitrogen as a purge gas for drinking water analysis. Laboratories who want to obtain accreditation for this method must complete all relevant regulatory requirements, including a completed on-site assessment and acceptable proficiency testing scores, prior to submitting an application. Both EPA method 524.2 and 524.3 require helium as the purge gas.

Using Hydrogen as a Carrier Gas Approved in ATP Case No. D12-0003

Changing the carrier gas is a major alteration to the method procedure, so the laboratory is required to re-validate the method's performance in their laboratory and perform an initial demonstration of capability using the new carrier gas. ELAP recommends reviewing the specific analytical method and the 2016 TNI standard, Volume 1 Module 4 sections 1.5 and 1.6 for validation and initial demonstration of capability criteria. While laboratories are not required to notify ELAP if they change carrier gas, documentation must be maintained demonstrating that the laboratory appropriately validated the method and meet the method's quality assurance and quality control criteria prior to conducting analysis on client samples.

In addition, utilizing hydrogen may require alterations to your laboratory's facility, and there may be specific requirements in the California Building Code and California Fire Code that apply. ELAP recommends consulting with your building operator or local regulatory agency to identify what your facility will need to address prior to making the change.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

Office of Ground Water and Drinking Water

June 2, 2022

MEMORANDUM

SUBJECT: Use of EPA Methods 524.3 and 524.4 without Refrigerated Autosamplers

FROM: Daniel P. Hautman, Deputy Director
Technical Support Center
Standards and Risk Management Division

DANIEL HAUTMAN

Digitally signed by DANIEL HAUTMAN
Date: 2022.06.02 14:27:36 -04'00'

TO: Regional Laboratory Certification Program Managers (LCPMs)
Regional Laboratory Directors
Regional Laboratory Certification Officers

Our Technical Support Center (TSC) is aware that there is an acute shortage of helium in the U.S. and that some laboratories analyzing drinking water compliance-monitoring samples are affected by that shortage. Among the methods that are most significantly impacted are "purge and trap" analyses for volatile organic contaminants (VOCs), particularly EPA Methods 524.2 and 524.3 due to the large volume of helium required for sparging. Based on this situation, we encourage impacted laboratories to consider switching to EPA Method 524.4, which is approved for drinking water compliance and uses nitrogen as the sparge gas.

TSC is aware that Method 524.4 specifies the use of a refrigerated autosampler (as does Method 524.3) and not all laboratories have this accessory. Consistent with data generated by EPA during the development of these methods, the refrigerated autosampler was specified to reduce degradation of *non-regulated* analytes within the scope of the method; importantly, those degradation concerns were not observed with any of the VOC analytes that are currently *regulated* under EPA's drinking water program (see Attachment 1). TSC is confident that Methods 524.3 and 524.4 will produce reliable results for regulated analytes even when a refrigerated autosampler is not being used. Accordingly, TSC encourages Regional and State Laboratory Certification Officers (COs) to exercise their judgement and apply flexibility when assessing laboratories for conformance with the subject method's refrigerated autosampler provisions.

Laboratories that are not currently certified/accredited to use Method 524.4 need to coordinate with their respective drinking water laboratory certification program and request Method 524.4 certification, prior to using that method to analyze drinking water compliance monitoring samples. Laboratories are not permitted to substitute nitrogen for helium as a modification to Method 524.2 or 524.3.

Laboratories running other gas chromatography (GC) methods for drinking water compliance-monitoring analyses, relying on helium as the GC carrier gas, are also likely impacted by the helium shortage. TSC reminds laboratories that under ATP Case No. D12-0003 (see Attachment 2), TSC acknowledged that hydrogen is acceptable as an alternate carrier gas for any approved GC method that originally identified helium as the carrier gas. Nitrogen, however, is not similarly effective and has not been identified as an appropriate alternative carrier gas. Please note that if a laboratory switches to hydrogen as their GC carrier gas, a new initial demonstration of capability (IDC) and updated SOP are required to document and validate acceptable performance.

Regional Laboratory Certification Program Managers are encouraged to share this memorandum with their State Laboratory Certification Programs, who should consider distributing the information within their certified laboratory community.

Please contact Michella Karapondo (Karapondo.michella@epa.gov), if you have questions or wish to further discuss this matter.

Attachment 1: "*Hydrolysis study of analytes within the scope of Methods 524.3 and 524.4*"
Attachment 2: "*ATP Case No. D12-0003 – The use of hydrogen as an alternate carrier gas in drinking water compliance methods.*"

Attachment 1

Hydrolysis study of analytes within the scope of Methods 524.3 and 524.4: Percent recovery at 60 ºC for proposed Targets Relative to Controls at 10 ºC

Targets Referenced to Internal Standard #1	%R	RSD	Targets Referenced to Internal Standard #2	%R	RSD	Targets Referenced to Internal Standard #3	%R	RSD
dichlorodifluoromethane	96.9	13	toluene	98.2	3.0	bromochloroiodomethane	94.0	9.0
chlorodifluoromethane	110	22	tetrachloroethene	93.9	2.3	bromobenzene	97.6	1.9
chloromethane	99.4	5.4	***trans-1,3-dichloropropene***	***71.1***	***4.5***	n-propylbenzene	98.6	4.2
vinyl chloride	100	7.4	ethyl methacrylate	102	3.0	1,1,2,2-tetrachloroethane	98.6	5.3
1,3-butadiene	95.0	3.2	1,1,2-trichloroethane	102	1.5	2-chlorotoluene	96.1	2.9
bromomethane	88.9	4.0	dibromochloromethane	99.7	3.6	1,3,5-trimethylbenzene	99.8	5.8
trichlorofluoromethane	97.4	9.0	1,3-dichloropropane	101	3.2	1,2,3-trichloropropane	100	5.5
diethyl ether	101	4.2	1,2-dibromoethane	102	6.5	4-chlorotoluene	95.8	1.1
1,1 dichloroethene	97.9	5.1	dichloroiodomethane	96.4	1.2	tert-butylbenzene	102	6.7
carbon disulfide	92.3	4.2	chlorobenzene	99.6	1.5	pentachloroethane	94.5	6.9
methyl iodide	95.5	3.3	ethyl benzene	95.2	2.3	1,2,4-trimethylbenzene	98.2	5.3
allyl chloride	***70.8***	***2.9***	1,1,1,2-tetrachloroethane	96.2	2.4	sec-butylbenzene	105	6.9
methylene chloride	99.7	5.1	p+m-xylene	95.6	1.3	p-isopropyltoluene	103	8.1
trans-1,2-dichloroethene	99.4	5.6	o-xylene	96.9	4.6	1,3-dichlorobenzene	96.4	2.6
methyl acetate	85.7	7.9	styrene	96.0	2.7	1,4-dichlorobenzene	96.5	2.5
hexane	88.5	7.0	bromoform	97.4	5.9	dibromoiodomethane	89.8	18
methyl-tert-butyl-ether	98.0	2.4	isopropylbenzene	98.0	3.3	n-butylbenzene	105	10
t- butyl alcohol	83.9	14				hexachloroethane	95.0	5.7
diisopropyl ether	100	2.9				1,2-dichlorobenzene	95.4	4.9
1,1-dichloroethane	99.4	6.3				chlorodiiodomethane	89.8	14
t- butyl ethyl ether	95.7	3.4				1,2-dibromo-3-chloropropan	93.7	8.2
cis-1,2-dichloroethene	100	5.8				***bromodiiodomethane***	***84.0***	***17***
bromochloromethane	101	3.2				hexachlorobutadiene	113	16
chloroform	101	5.8				1,2,4-trichlorobenzene	101	9.4
carbon tetrachloride	97.7	4.5				naphthalene	97.5	5.0
tetrahydrofuran	97.6	5.9				1,2,3-trichlorobenzene	101	6.0
1,1,1-trichloroethane	97.6	4.8						
1,1-dichloropropene	98.3	7.1						
1-chlorobutane	97.1	3.2						
benzene	101	6.3						
t- amyl methyl ether	91.8	2.4						
1,2-dichloroethane	102	4.1						
trichloroethene	97.6	5.5						
t- amyl ethyl ether	***82.3***	***3.4***						
dibromomethane	101	2.7						
1,2-dichloropropane	101	4.8						
bromodichloromethane	99.0	4.5						
cis-1,3-dichloropropene	***75.2***	***5.8***						

%R = percent recovery

RSD = relative standard deviation

Federally regulated analyte under EPA's drinking water program

Unregulated analyte "impacted" by thermal degradation

Attachment 2

ATP Case No. D12-0003 – The use of hydrogen as an alternate carrier gas in drinking water compliance methods

MEMORANDUM

DATE: March 19, 2012

SUBJECT: The use of hydrogen as an alternate carrier gas in drinking water compliance methods.

FROM: Steven C. Wendelken PhD
ATP coordinator
Technical Support Center

RE: ATP Case No. D12-0003

Per the terms of the Alternate Test Procedure (ATP) program, the Office of Ground Water and Drinking Water's Technical Support Center (OGWDW/TSC) has determined that hydrogen is an acceptable carrier for gas chromatography and may be used in place of helium in drinking water compliance methods. This replacement is allowed as long as all of the quality control criteria in the method are met. Please consult your instrument manufacturer for any special instructions regarding this conversion.

We appreciate your interest in the development of environmental monitoring methods. If you have any questions regarding this alternate test procedure (ATP Case No. D12-0003), please contact Steve Wendelken by e-mail at: wendelken.steve@epa.gov or by telephone at: 513-569-7491.

Sincerely,

Steven C. Wendelken PhD
U.S. EPA, OGWDW-TSC
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45219
Phone: (513) 569-7491
Fax: (513) 569-7837
wendelken.steve@epa.gov

cc:
ATP Coordinators (all Regions)
Danielle Carter, CSC, SCC