New Reference Mixes for Determination of Chlorinated Disinfection Byproducts, Chlorinated Solvents, or Halogenated Pesticides in Drinking Water

by John Lidgett, Analytical Reference Materials Technical Specialist

- Complete set of high concentration reference materials for US EPA Method 551.1.
- Target pesticides/herbicides at equal concentration, for GC/MS analysis.
- Chloral hydrate and metribuzin offered as separate solutions, for assured stability.

Chlorine has been used to disinfect drinking water for many years. Chlorinating agents, however, can form harmful and potentially carcinogenic byproducts with organic compounds in water, and this potential led to US Environmental Protection Agency regulation in 1979.[1] Extensive research has been done on the origination of disinfection byproducts (DBPs), and on preventing their formation. DBPs can form by reaction of chlorine with naturally present organic compounds in water, such as humic acid or fulvic acid - organic compounds found in water as a result of decomposition of plant matter. Disinfection byproducts include 3 groups of compounds: trihalomethanes (THMs), haloacetonitriles, and a mixed group that includes chloral hydrate, chloropicrin, and chloropropanones. Many other DBPs, including haloacetic acids, haloacetaldehydes, cyanogen halides, aldehydes, ketoacids, chlorite, bromate, and other organic and inorganic compounds also have been identified in chlorinated or ozonated drinking water.[2]

Several US EPA methods regulate the monitoring of drinking water, including methods 502.2, 524.1, 551.1, and 552.2. In addition to THMs, Method 551.1 is followed for monitoring chlorinated solvents and halogenated pesticides/herbicides. EPA Method 551 requires liquid-liquid extraction with methyl-*tert*-butyl ether (MTBE) as a primary extraction solvent and analysis by GC, using electron capture detection (ECD). The latest version of Method 551, Method 551.1, allows pentane to be used as the extraction solvent if chloral hydrate is not being analyzed. Qualitative confirmation of the target compounds is required by GC/MS analysis or by GC on two dissimilar columns. The listed primary analytical column is a bonded methyl polysiloxane stationary phase Restek column, Rtx®-1 (30m, 0.25mm ID, 1.0μm film, cat.# 10153); the listed confirmation column is a bonded 6% cyanopropylphenyl / 94% dimethyl polysiloxane stationary phase Restek column, Rtx®-1301 (30m, 0.25mm ID, 1.0μm film, cat.# 16053).

Restek chemists have formulated three new calibration mixes, Disinfection Byproducts & Chlorinated Solvents Mix (cat.# 30615), Disinfection Byproducts Mix (cat.# 30616), and Method 551.1 Pesticide/Herbicide Mix (cat.# 32438), to include all but two Method 551.1 target compounds, based on enhanced stability and the testing requirements of our customers. We prepare the three new solutions in acetone, because methanol causes degradation of most haloacetonitriles, and acetone should be used for primary dilution in preparing working solutions. Bromochloroacetonitrile, a target compound we include in two of our new mixes (Disinfection Byproducts & Chlorinated Solvents Mix, Disinfection Byproducts Mix) is not available commercially at purity higher than 89%. Dichloroacetonitrile and dibromoacetonitrile are both target compounds in the calibration mixes and impurities in bromochloroacetonitrile, at 0.5 to 2.2%. After careful review, we determined that Method 551.1 allows a 4% concentration error and, based on this information, we have included bromochloroacetonitrile in both reference materials after compensating for the impurities.

Because chloral hydrate is unstable, due to hydrogen-bond interactions with halide ions, we offer it as a separate solution. After several months of stability studies, using various solvents, we determined that chloral hydrate should be offered in acetonitrile, and we seal the reference material in light-resistant ampuls as defined in the United States Pharmacopoeia (USP). When using chloral hydrate all working solutions and glassware should be free of alkaline substances and the reference material should be stored away from heat, because heating chloral hydrate with alkali produces chloroform. Note that chloral hydrate is a hypnotic depressant included in Schedule IV of the Controlled Substance Act. We have the required license and exception approval to offer chloral hydrate as a reference material.

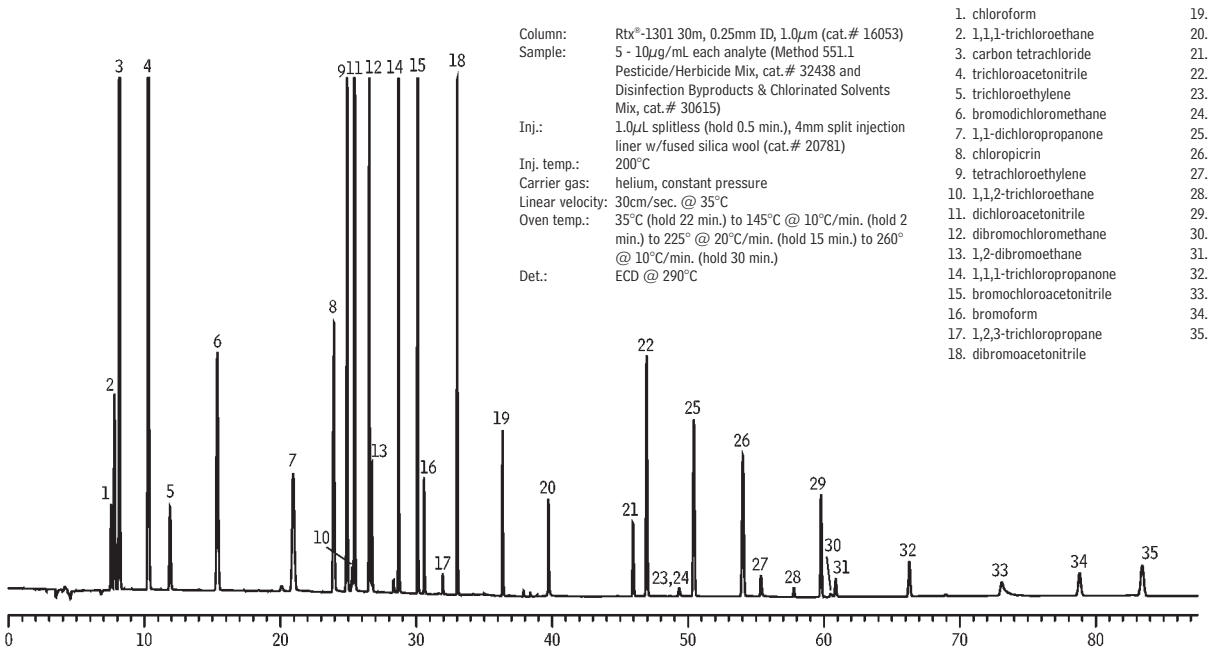
For stability, we also offer another compound in this interest group, metribuzin, as a separate mix (cat.# 32436). In earlier studies we determined that metribuzin could react with certain pesticides/herbicides at high concentration.

We offer an internal standard, bromofluorobenzene, and a surrogate standard, decafluorobiphenyl, in acetone, per method recommendations. The method recommends the use of a laboratory performance check (LPC) solution in MTBE, the extraction solvent. The check solution is a mix of method analytes used to evaluate the performance of the instrument. The parameters evaluated are instrument sensitivity, chromatographic performance, column performance, and analyte breakdown. Special care must be taken when analyzing endrin, a component in our new pesticide/herbicide mix, because it can break down to aldo and keto derivatives on contact with active metal sites in the injection port. The analyzed value of each compound in the check solution should be 95% to 105% of its expected value. For analysts using pentane as the extraction solvent, we offer the laboratory performance check solution in pentane. Analysis of the LPC solution is especially difficult because of the substantial range in concentration (0.2 to 83 μg/mL) of the components. Because of the high sensitivity and narrow range of linear detection of the ECD, and the possibility of coelution of solvent impurities with some of the target compounds, we use high purity MTBE and pentane in preparing the LPC solutions.

Our complete set of reference materials for determining Method 551.1 target compounds is listed on page 17. If you are analyzing for disinfection byproducts, chlorinated solvents, or chlorinated pesticides/herbicides, we highly recommend these carefully prepared standards. We also offer Rtx®-1 and Rtx®-1301 capillary columns, which are ideal for the analysis, and are listed in Method 551.1.

References
1. *US Environmental Protection Agency National Interim Primary Drinking Water Regulations: Control of Trihalomethanes in Drinking Water, Final Rule* Fed. Reg. 44 (231): 68624 (1979).
2. Yue Feng Xie, *Disinfection By-Product Analysis in Drinking Water* American Laboratory, Nov. 2000, p. 50.

Figure 1 Use an Rtx®-1301 column for optimal separation of disinfection byproducts.



Method 551.1 Pesticide/Herbicide Mix

alachlor
atrazine
bromacil
cyanazine (Bladex)
endrin
endrin aldehyde
endrin ketone
g-BHC (Lindane)
heptachlor
heptachlor epoxide (isomer B)
hexachlorobenzene
hexachlorocyclopentadiene
methoxychlor
metolachlor
simazine
trifluralin

1,000µg/mL each in acetone, 1mL/ampul
cat. # 32438 (ea.)

Disinfection by-Product and Chlorinated Solvents Mix

bromochloroacetonitrile
bromodichloromethane
bromoform
carbon tetrachloride
chloroform
chloropicrin
dibromoacetonitrile
dibromochloromethane
1,2-dibromo-3-chloropropane[DBCP]
1,2-dibromoethane[EDB]
dichloroacetonitrile
1,1-dichloro-2-propanone
tetrachloroethylene
trichloroacetonitrile
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethylene
1,2,3-trichloropropane
1,1,1-trichloro-2-propanone

2000µg/mL each in acetone, 1mL/ampul
cat. # 30615 (ea.)

Disinfection by-Product Mix

bromochloroacetonitrile
chloropicrin
dibromoacetonitrile
dichloroacetonitrile
1,1-dichloro-2-propanone
trichloroacetonitrile
1,1,1-trichloro-2-propanone

2000µg/mL each in acetone, 1mL/ampul
cat. # 30616 (ea.)

Method 551.1 MTBE Lab Performance Check Mix

alachlor	83µg/mL	endrin	30
g-BHC (Lindane)	0.2	hexachlorocyclopentadiene	20
bromacil	83	trichloroethylene	30
bromodichloromethane	30		

In methyl *tert*-butyl ether, 1mL/ampul
cat. # 32440 (ea.)

Laboratory Performance Check Solution/ Pentane Extract

alachlor	83µg/mL	endrin	30
g-BHC	0.2	hexachlorocyclopentadiene	20
bromacil	83	trichloroethylene	30
bromodichloromethane	30		

In pentane, 1mL/ampul
cat. # 32442 (ea.)

Metribuzin

metribuzin

1,000µg/mL in acetone, 1mL/ampul
1,000 cat. # 32436 (ea.)

551.1 Internal Standard

1-bromo-4-fluorobenzene

1,000µg/mL in acetone, 1mL/ampul
cat. # 31854 (ea.)

551.1 Surrogate Standard

decafluorobiphenyl

1,000µg/mL in acetone, 1mL/ampul
cat. # 31855 (ea.)

Chloral Hydrate

chloral hydrate

1,000µg/mL in acetonitrile, 1mL/ampul
cat. # 30609 (ea.)

Rtx®-1 Column (fused silica)

(Crossbond® 100% dimethyl polysiloxane)
Temp. limits: -60 to 320/340°C

ID	df (µm)	length	cat. #
0.25mm	1.00	30-Meter	10153

Rtx®-1301 Column (fused silica)

(Crossbond® 6% cyanopropylphenyl/94% dimethyl polysiloxane)
Temp. limits: -20 to 260°C

ID	df (µm)	length	cat. #
0.25mm	1.00	30-Meter	16053

Renzo Brun, Restek France

Vive la France!

In addition to the traditional seasonal celebrations, 200-plus Restek employee-owners had something extra to commemorate this past December: Restek France has been meeting chromatographers' needs for Restek products and Plus 1™ service for ten years! Félicitations to everyone at Restek France—and best wishes for many more achievements to come.

Universal "Y" Press-Tight® Connectors

- Split sample flow onto two columns.
- Split a single column flow to two detectors—perform confirmation analysis with a single injection.
- Fit column ODs from 0.33–0.74mm (Restek 0.1mm–0.53mm ID).

Description	ea.	3-pk.
"Y" Press-Tight® Connector	20405	20406
Siltek®-treated "Y" Press-Tight® Connector	20485	20486