# Development of U.S. EPA Method 551.1

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## Abstract

**As initially written, U.S. EPA method 551 included 12 chlorination disinfection byproducts and six halogenated solvents. This method is significantly revised as U.S. EPA method 551.1 to include 12 commonly observed chlorination disinfection byproducts, eight halogenated organic solvents, and 17 pesticides and herbicides. The applicability of the revised method has increased as a consequence of the larger analyte list. In addition, built into the method is the flexibility to choose only those analytes from the list which are critical to a specific application. Several procedural modifications are incorporated into the method, such as simplifying sample preservation, specifying a different salting agent, allowing the conditional use of pentane as an alternate extraction solvent, and recommending simultaneous confirmation analysis. Data are presented that illustrate the importance of including these method modifications into U.S. EPA method 551.1.**

## Introduction

U.S. EPA method 551 (1) was originally written with the focus primarily directed toward disinfection byproducts (DBPs) and a select group of commonly used halogenated solvents. This method has been expanded to include 17 pesticides and herbicides and two additional halogenated solvents. These additional analytes were selected based on their regulatory status and as a means to consolidate several analytes from various methodologies into one U.S. EPA method.

Several procedural changes have also been included to improve the method. One significant change involves the use of a dry phosphate buffer rather than hydrochloric acid (HCl) to acidify the sample matrix. Sample matrix acidification is required in order to inhibit the base-catalyzed degradation of the haloacetonitriles. Due to shipping concerns with concentrated HCl and the cumbersome procedure of acidification in the field, including the dry phosphate buffer in the sample vial that is shipped to the sampling site is considerably more practical. In addition, pentane has been specified as an alternate to methyl-*t*-butyl ether (MtBE) as the extraction solvent, and sodium sulfate ($Na_2SO_4$) rather than sodium chloride (NaCl) has been recommended as the extraction salt. The change to $Na_2SO_4$ was warranted due to the influence of trace bromide ion impurities found in NaCl, which were shown to increase sample concentrations of brominated DBPs (2,3). Finally, a procedure detailing a simultaneous confirmation analysis has been included.

The development of U.S. EPA method 551.1 (4) is discussed. Analyte stability studies in buffered aqueous matrices illustrate the importance of matrix acidification. Volatility experiments were conducted which indicated the importance of specifying careful sample handling procedures in order to reduce analyte losses.

## Experimental

### Additional method analytes and analysis conditions

Table I shows the revised analyte list for U.S. EPA method 551.1, including Chemical Abstracts Service (CAS) registry numbers. Initially, a gas chromatography (GC) oven temperature program needed to be devised that could effectively resolve all of these method analytes within a reasonable amount of time. This program needed to take into consideration the fact that all the DBPs elute from the capillary GC column between 35 and 145°C, and the pesticides and herbicides do not elute until the oven temperature is at least 225°C. Consequently, an oven temperature program needed to be tailored that initially allowed for the proper resolution of all the DBPs, then rapidly increased to a high temperature to allow for the proper resolution of the pesticides and herbicides. The final program afforded simultaneous confirmation analysis without the need for cryogenic cooling and effectively resolved all the analytes on the primary column and all the analytes except atrazine and simazine on the confirmation column.

For the primary column, a 30-m × 0.25-mm-i.d. fused-silica capillary column with chemically bonded methyl polysiloxane phase was used (DB-1, 1.0-µm film thickness or equivalent)

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(J&W Scientific, Folsom, CA). The linear velocity of the helium carrier gas was 25 cm/s at 35°C. The column oven was temperature-programmed as follows: held at 35°C for 22 min, then increased to 145°C at 10°C/min and held for 2 min, then increased to 225°C at 20°C/min and held for 15 min, then increased to 260°C at 10°C/min and held for 30 min or until all expected compounds had eluted.

As the confirmation column, a 30-m × 0.25-mm-i.d. fused-silica capillary column with chemically bonded 6% cyanopropyl-phenyl and 94% dimethyl polysiloxane phase was used (Rtx-1301, 1.0-µm film thickness or equivalent) (Restek, Bellefonte, PA). The linear velocity of the helium carrier gas was 25 cm/s at 35°C. The column oven was temperature-programmed exactly as indicated for the primary column. The same temperature program was utilized to allow for simultaneous confirmation analysis.

A splitless mode injector (Hewlett-Packard, Wilmington, DE) with the split delayed to 0.50 min was used at a temperature of 200°C. A linearized nickel[63] electron-capture detector (ECD) (Hewlett-Packard) was also used at a temperature of 290°C. The makeup gas was 95% argon and 5% methane, and the flow rate was 30mL/min.

As a result of including these additional method analytes, the

**Table I. U.S. EPA 551.1 Method Analytes**

| | Analyte | CAS no. |
|---|---|---|
| (DBPs): | | |
| Trihalomethanes | Chloroform | 67-66-3 |
| | Bromodichloromethane | 75-27-4 |
| | Bromoform | 75-25-2 |
| | Dibromochloromethane | 124-48-1 |
| Haloacetonitriles | Bromochloroacetonitrile | 83463-62-1 |
| | Dibromoacetonitrile | 3252-43-5 |
| | Dichloroacetonitrile | 3018-12-0 |
| | Trichloroacetonitrile | 545-06-2 |
| Other DBPs | Chloral hydrate | 75-87-6 |
| | Chloropicrin | 76-06-2 |
| | 1,1-Dichloro-2-propanone | 513 -88-2 |
| | 1,1,1-Trichloro-2-propanone | 918-00-3 |
| Chlorinated/halogenated solvents: | | |
| | Carbon tetrachloride | 56-23-5 |
| | 1,2-Dibromo-3-chloropropane (DBCP) | 96-12-8 |
| | 1,2-Dibromoethane (EDB) | 106-93-4 |
| | Tetrachloroethylene | 127-18-4 |
| | 1,1,1-Trichloroethane | 71-55-6 |
| | *1,1,2-Trichloroethane | 79-00-5 |
| | Trichloroethylene | 79-01-6 |
| | *1,2,3-Trichloropropane | 96-18-4 |
| Pesticides/herbicides: | | |
| | *Alachlor | 15972-60-8 |
| | *Atrazine | 1912-24-9 |
| | *Bromacil | 314-40-9 |
| | *Cyanazine | 21725-46-2 |
| | *Endrin | 72-20-8 |
| | *Endrin aldehyde | 7421-93-4 |
| | *Endrin ketone | 53494-70-5 |
| | *Heptachlor | 76-44-8 |
| | *Heptachlor epoxide | 1024-57-3 |
| | *Hexachlorobenzene | 118-74-1 |
| | *Hexachlorocyclopentadiene | 77-47-4 |
| | *Lindane (γ-BHC) | 58-89-9 |
| | *Methoxychlor | 72-43-5 |
| | *Metolachlor | 51218-45-2 |
| | *Metribuzin | 21087-64-9 |
| | *Simazine | 122-34-9 |
| | *Trifluralin | 1582-09-8 |

*Analytes added as part of the revised U.S. EPA method 551.1.

**Table II. Analyte Retention Times**

| Analyte | Primary column retention time (min) | Confirmation column retention time (min) |
|---|---|---|
| Chloroform | 7.04 | 7.73 |
| 1,1,1-Trichloroethane | 8.64 | 7.99 |
| Carbon tetrachloride | 9.94 | 8.36 |
| Trichloroacetonitrile | 10.39 | 10.35 |
| Dichloroacetonitrile | 12.01 | 25.21 |
| Bromodichloromethane | 12.42 | 15.28 |
| Trichloroethylene | 12.61 | 11.96 |
| Chloral hydrate | 13.41 | NR* |
| 1,1-Dichloro-2-propanone | 14.96 | 20.50 |
| 1,1,2-Trichloroethane | 19.91 | 25.01 |
| Chloropicrin | 23.10 | 23.69 |
| Dibromochloromethane | 23.69 | 26.32 |
| Bromochloroacetonitrile | 24.03 | 29.86 |
| 1,2-Dibromoethane (EDB) | 24.56 | 26.46 |
| Tetrachloroethylene | 26.24 | 24.77 |
| 1,1,1-Trichloro-2-propanone | 27.55 | 28.47 |
| Bromoform | 29.17 | 30.36 |
| Dibromoacetonitrile | 29.42 | 32.77 |
| 1,2,3-Trichloropropane | 30.40 | 31.73 |
| 1,2-Dibromo-3-chloropropane (DBCP) | 35.28 | 36.11 |
| Hexachlorocyclopentadiene | 40.33 | 39.53 |
| Trifluralin | 45.17 | 45.43 |
| Simazine | 46.27 | 48.56† |
| Atrazine | 46.55 | 48.56† |
| Hexachlorobenzene | 47.39 | 46.47 |
| Lindane (gamma-BHC) | 47.95 | 49.68 |
| Metribuzin | 50.25 | 53.92 |
| Bromacil | 52.09 | 59.60 |
| Alachlor | 52.25 | 54.38 |
| Cyanazine | 53.43 | 59.89 |
| Heptachlor | 53.72 | 53.15 |
| Metolachlor | 55.44 | 57.07 |
| Heptachlor epoxide | 58.42 | 59.05 |
| Endrin | 64.15 | 65.24 |
| Endrin aldehyde | 65.46 | 71.56 |
| Endrin ketone | 72.33 | 81.28 |
| Methoxychlor | 73.53 | 76.73 |
| Surrogate: decafluorobiphenyl | 36.35 | 36.28 |
| Internal standard: bromofluorobenzene | 31.00 | 31.30 |

* There is no retention time for this analyte because it did not elute chromatographically into a discreet band on the Rtx-1301 column.
† Atrazine and simazine coeluted on the confirmation column.

chromatographic analysis time was increased to approximately 1.5 h. Consequently, a simultaneous confirmation analysis is recommended as a means to process samples efficiently. In order to perform simultaneous confirmation, the GC must be equipped with a second ECD. Using a two-hole ferrule, both the primary and confirmation capillary columns are inserted into a single injection port. Alternatively, an uncoated 1-m length of deactivated capillary column can be installed into the injection port and subsequently attached to the primary and confirmation columns using a Y-connector. This alternate procedure may, however, result in poorer detection limits because the sample deposited on the precolumn is split into two columns. By performing a simultaneous confirmation, a complete primary quantitative and secondary analyte confirmation analysis is conducted from a single injection.

### Matrix preservation and acidification

The haloacetonitriles included in this method are susceptible to base-catalyzed degradation; therefore, field sample acidification is required. Method 551 includes a procedure which

**Table III. Detection Limits on the Primary Column**

| | MtBE extracted, $NH_4Cl$ preserved reagent water | | | | | |
|---|---|---|---|---|---|---|
| Analyte | Fortified concentration (µg/L) | Observed concentration* (µg/L) | Average % recovery | RSD (%) | MDL† (µg/L) | EDL‡ (µg/L) |
| Alachlor | 0.327 | 0.384 | 117 | 2.13 | 0.025 | 0.500 |
| Atrazine | 0.633 | 0.764 | 121 | 3.56 | 0.082 | 0.324 |
| Bromacil | 0.094 | 0.099 | 105 | 10.05 | 0.030 | 0.055 |
| Bromochloroacetonitrile | 0.010 | 0.011 | 110 | 5.42 | 0.002 | 0.009 |
| Bromodichloromethane | 0.010 | 0.012 | 120 | 7.50 | 0.003 | 0.005 |
| Bromoform | 0.010 | 0.018 | 180 | 8.12 | 0.004 | 0.006 |
| Carbon tetrachloride | 0.010 | 0.011 | 110 | 6.32 | 0.002 | 0.004 |
| Chloral hydrate | 0.025 | 0.029 | 116 | 5.61 | 0.005 | 0.011 |
| Chloropicrin | 0.010 | 0.009 | 90 | 7.65 | 0.002 | 0.014 |
| Chloroform | 0.050 | 0.054 | 108 | 34.04 | 0.055 | 0.075 |
| Cyanazine | 0.567 | 0.757 | 134 | 13.93 | 0.316 | 0.685 |
| Dibromoacetonitrile | 0.010 | 0.016 | 160 | 12.78 | 0.006 | 0.010 |
| Dibromochloromethane | 0.010 | 0.011 | 110 | 4.55 | 0.001 | 0.007 |
| 1,2-Dibromo-3-chloropropane | 0.010 | 0.020 | 200 | 15.15 | 0.009 | 0.009 |
| 1,2-Dibromoethane | 0.010 | 0.020 | 200 | 12.54 | 0.008 | 0.008 |
| Dichloroacetonitrile | 0.010 | 0.009 | 90 | 4.28 | 0.001 | 0.005 |
| 1,1-Dichloro-2-propanone | 0.010 | 0.011 | 110 | 6.22 | 0.002 | 0.007 |
| Endrin | 0.016 | 0.023 | 144 | 2.57 | 0.002 | 0.011 |
| Endrin aldehyde | 0.022 | 0.023 | 105 | 2.25 | 0.002 | 0.010 |
| Endrin ketone | 0.016 | 0.016 | 100 | 5.14 | 0.002 | 0.020 |
| Heptachlor | 0.047 | 0.062 | 132 | 43.65 | 0.081 | 0.081 |
| Heptachlor epoxide | 0.044 | 0.050 | 114 | 1.64 | 0.002 | 0.030 |
| Hexachlorobenzene | 0.006 | 0.006 | 100 | 5.44 | 0.001 | 0.006 |
| Hexachlorocyclopentadiene | 0.019 | 0.019 | 100 | 31.81 | 0.018 | 0.022 |
| Lindane (γ-BHC) | 0.009 | 0.015 | 167 | 9.89 | 0.004 | 0.016 |
| Methoxychlor | 0.063 | 0.057 | 90 | 4.85 | 0.008 | 0.046 |
| Metolachlor | 0.219 | 0.254 | 116 | 3.20 | 0.024 | 0.146 |
| Metribuzin | 0.062 | 0.100 | 161 | 12.45 | 0.037 | 0.037 |
| Simazine | 0.625 | 0.794 | 127 | 5.95 | 0.142 | 0.431 |
| Tetrachloroethylene | 0.010 | 0.012 | 120 | 5.04 | 0.002 | 0.004 |
| Trichloroacetonitrile | 0.010 | 0.010 | 100 | 5.31 | 0.002 | 0.004 |
| 1,1,1-Trichloroethane | 0.010 | 0.013 | 130 | 12.35 | 0.005 | 0.005 |
| 1,1,2-Trichloroethane | 0.140 | 0.124 | 89 | 3.27 | 0.012 | 0.040 |
| Trichloroethylene | 0.010 | 0.008 | 80 | 8.68 | 0.002 | 0.008 |
| 1,2,3-Trichloropropane | 0.156 | 0.137 | 88 | 1.95 | 0.008 | 0.028 |
| 1,1,1-Trichloro-2-propanone | 0.010 | 0.027 | 270 | 20.53 | 0.016 | 0.016 |
| Trifluralin | 0.022 | 0.026 | 118 | 3.89 | 0.003 | 0.010 |
| Surrogate: decafluorobiphenyl | 10.0 | 10. 8 | 108 | .38 | | |

* Based on the analysis of eight replicate MtBE sample extracts.
† MDL designates the statistically derived MDL and was calculated by multiplying the standard deviation of the eight replicates by the student's *t*-value (2.998), appropriate for a 99% confidence level and a standard deviation estimate with a degree of freedom one less than the number of replicates.
‡ Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal-to-noise ratio of approximately 5, whichever is greater.

involved dropwise addition of concentrated HCl to the sample matrix until pH 4.5 is attained. Due to the presence of carbonate and other dissolved salts in field sample matrices which create a natural buffering effect, the volume of concentrated HCl required to adjust this pH was site-specific and seasonally dependent. Consequently, a trained field sampling team would need to carefully monitor the matrix pH after each dropwise addition of HCl. If the carbonic acid endpoint at pH 4.2 was surpassed, the sample pH would fall rapidly, and the integrity of the sample would be compromised. In addition, to ensure that a consistent high-quality concentrated HCl is used by the sampling team, concentrated HCl may need to be shipped with the sampling kit. This would require special packaging conforming to Department of Transportation (DOT) shipping regulations as well as field handling precautions, due to the corrosive nature of HCl. A preferred alternative to this HCl procedure would include the addition of a dry buffering agent placed in the sampling vial in the laboratory prior to shipping the kit to the field sampling site. This procedure would remove many of the potential variables that would be introduced by the sampling team and surmount the shipping concerns pertaining to concentrated HCl.

**Table IV. Detection Limits on the Confirmation Column**

| | MtBE extracted, $NH_4Cl$ preserved reagent water | | | | | |
|---|---|---|---|---|---|---|
| Analyte | Fortified concentration (µg/L) | Observed concentration* (µg/L) | Average recovery (%) | RSD (%) | MDL† (µg/L) | EDL‡ (µg/L) |
| Alachlor | 0.109 | 0.107 | 98 | 1.70 | 0.005 | 0.076 |
| Bromacil | 0.094 | 0.134 | 143 | 11.65 | 0.047 | 0.071 |
| Bromochloroacetonitrile | 0.010 | 0.008 | 80 | 9.49 | 0.002 | 0.015 |
| Bromodichloromethane | 0.010 | 0.012 | 120 | 4.34 | 0.002 | 0.006 |
| Bromoform | 0.010 | 0.015 | 150 | 29.51 | 0.013 | 0.013 |
| Carbon tetrachloride | 0.010 | 0.011 | 110 | 18.70 | 0.006 | 0.006 |
| Chloropicrin | 0.010 | § | § | § | § | 0.062 |
| Chloroform | 0.010 | 0.059 | 590 | 2.82 | 0.005 | 0.008 |
| Cyanazine | 0.189 | 0.279 | 148 | 7.56 | 0.063 | 0.065 |
| Dibromoacetonitrile | 0 010 | 0.010 | 100 | 4.87 | 0.001 | 0.007 |
| Dibromochloromethane | 0.010 | 0.021 | 210 | 29.30 | 0.018 | 0.018 |
| 1,2-Dibromo-3-chloropropane | 0.010 | 0.020 | 200 | 9.95 | 0.006 | 0.024 |
| 1,2-Dibromoethane | 0.010 | 0.039 | 390 | 6.44 | 0.007 | 0.007 |
| Dichloroacetonitrile | 0.010 | 0.010 | 100 | 4.11 | 0.001 | 0.003 |
| 1,1-Dichloro-2-propanone | 0.010 | 0.009 | 90 | 11.65 | 0.003 | 0.015 |
| Endrin | 0.016 | 0.025 | 156 | 4.09 | 0.003 | 0.015 |
| Endrin aldehyde | 0.022 | 0.034 | 155 | 22.45 | 0.023 | 0.030 |
| Endrin ketone | 0.047 | 0.049 | 104 | 5.49 | 0.008 | 0.047 |
| Heptachlor | 0.016 | 0.018 | 113 | 3.79 | 0.002 | 0.010 |
| Heptachlor epoxide | 0.044 | 0.079 | 180 | 84.71 | 0.202 | 0.202 |
| Hexachlorobenzene | 0.006 | 0.006 | 100 | 16.47 | 0.003 | 0.011 |
| Hexachlorocyclopentadiene | 0.019 | § | § | § | | 0.327 |
| Lindane (γ-BHC) | 0.009 | 0.011 | 122 | 6.09 | 0.002 | 0.009 |
| Methoxychlor | 0.188 | 0.221 | 118 | 3.53 | 0.023 | 0.041 |
| Metolachlor | 0.219 | 0.280 | 128 | 1.45 | 0.012 | 0.268 |
| Metribuzin | 0.062 | 0.076 | 123 | 2.17 | 0.005 | 0.013 |
| Simazine/atrazine | 1.26** | 1.619 | 129 | 2.48 | 0.121 | 0.629 |
| Tetrachloroethylene | 0.010 | 0.012 | 120 | 6.97 | 0.002 | 0.003 |
| Trichloroacetonitrile | 0.010 | 0.006 | 60 | 16.01 | 0.003 | 0.010 |
| 1,1,1-Trichloroethane | 0.010 | 0.020 | 200 | 19.22 | 0.012 | 0.012 |
| 1,1,2-Trichloroethane | 0.140 | 0.133 | 95 | 3.40 | 0.014 | 0.020 |
| Trichloroethylene | 0.010 | 0.009 | 90 | 13.77 | 0.004 | 0.007 |
| 1,2,3-Trichloropropane | 0.156 | 0.160 | 103 | 3.11 | 0.015 | 0.114 |
| 1,1,1-Trichloro-2-propanone | 0.010 | 0.011 | 110 | 7.11 | 0.002 | 0.010 |
| Trifluralin | 0.022 | 0.024 | 109 | 3.07 | 0.002 | 0.006 |
| Surrogate: decafluorobiphenyl | 10.0 | 10.6 | 106 | 1.78 | | |

* Based on the analysis of eight replicate MtBE sample extracts.
† MDL designates the statistically derived MDL and was calculated by multiplying the standard deviation of the eight replicates by the student's *t*-value (2.998), appropriate for a 99% confidence level and a standard deviation estimate with a degree of freedom one less than the number of replicates.
‡ Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal-to-noise ratio of approximately 5, whichever is greater.
§ No peak was detected for the eight replicate MDL determinations.
**The concentrations of atrazine and simazine were added together for this determination because these two peaks coeluted on the confirmation column.

Initial experiments were conducted using a pH 6.0 phosphate buffer. The pH 6.0 dry phosphate buffer was a homogeneous mixture of 13% sodium phosphate, dibasic ($Na_2HPO_4$) and 87% potassium phosphate, monobasic ($KH_2PO_4$). An aqueous buffered pH of 6.0 was attained by dissolving 1.0 g of this dry buffer in 100 mL of water. By using this buffer salt, an aqueous matrix stability study was conducted using reagent water and local tap water which were dechlorinated and fortified with method analytes. Triplicate analyses were conducted on samples extracted on days 0, 7, 14, and 20. During this storage study, the aqueous samples were held in a refrigerator at 4°C and were protected from light.

Most analytes were stable; however, significant losses were observed in trichloroacetonitrile (TCAN) by day 7. TCAN losses by day 20 are illustrated in Figure 3. As a result of this pH 6.0 stability study, it became apparent that further pH reduction of the matrix was required to stabilize TCAN from base-catalyzed degradation. A buffering salt combination that would yield a matrix pH of 4.5–5.0 would have been ideal. Experiments were initiated with buffering systems containing succinic acid and sodium succinate or oxalic acid and sodium oxalate, but both of these proved to be problematic. In each case, the nondissociated acid component of the buffer was an organic compound that could be extracted with the solvent and subsequently became a chromatographic interferant. It was concluded that the buffering salt needed to be an inorganic salt, and attention was refocused on the phosphate buffer. By adjusting the ratio of the phosphate salts to 2.5% $Na_2HPO_4$ and 97.5% $KH_2PO_4$, a pH of 5.3 was achieved. By using this modified phosphate buffer, a second aqueous matrix stability study was conducted again using reagent water and local tap water which were dechlorinated and fortified with method analytes. Triplicate analyses were conducted on samples extracted on days 0, 7, 14, and 21. During this storage study, the aqueous samples were again held in a refrigerator at 4°C and were protected from light.

### Sample handling and analyte volatility

As part of the development of method 551.1, analyte volatility experiments were conducted. These volatility experiments were designed to examine the impact that sample transfers from one sampling vial to a second vial would have on analyte recoveries. These transfers seem logical because samples are received in 60-mL vials and 50 mL of sample is required for extraction. Typically, an analyst may be inclined to zero a top loading balance with a clean, empty 60-mL vial and then transfer the sample from the original vial used for sample collection until a weight of 50 g (nearly equivalent to 50 mL) is attained. Another possibility would involve using a graduated cylinder to measure the 50 mL volume and then pouring the measured sample into a clean 60-mL vial, actually accounting for two sample transfers. The original method 551 outlined a procedure of extracting the sample in the original sampling vial without performing such sample transfers, but the text did not explain the rationale behind this procedure. Several laboratories

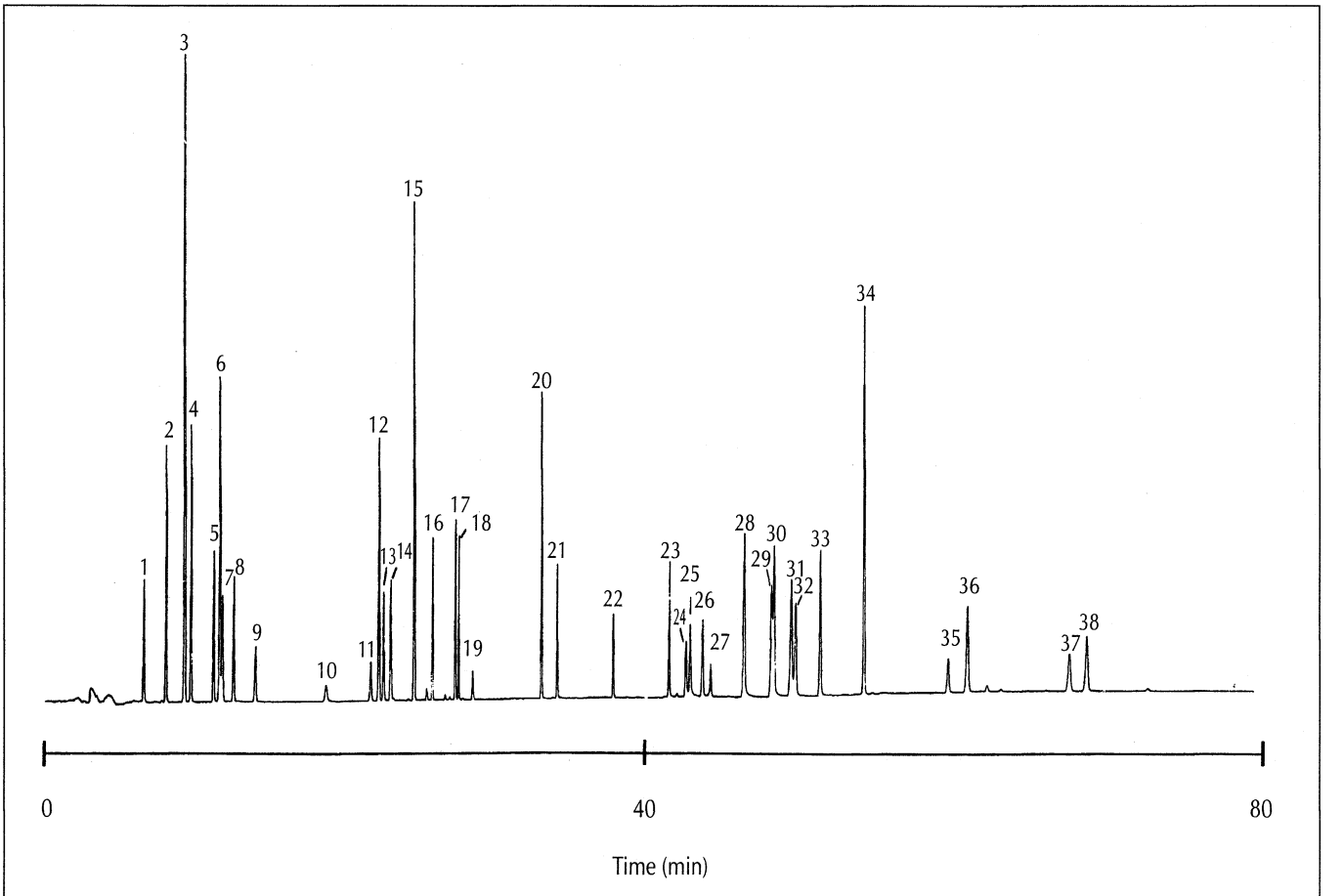


**Figure 1.** Analyte retention, primary DB-1 column.

inquired about the acceptability of performing such sample transfers as a means to accurately measure sample volume, and therefore specific experiments were conducted to evaluate analyte losses when these transfers were performed.

A set of 12 identical fortified reagent water samples were prepared and divided into four experimental groups; each group contained three samples for subsequent triplicate extraction and analysis. Only the more volatile DBPs and halogenated solvents were included in this study because the pesticides and herbicides are not volatile. The first group of three samples was used for calibration with no sample transfers performed once the matrices had been fortified. This first group acted as the control because it was presumed that minimal loss would occur if no sample transfers occurred. The second group of three samples was transferred from the vial in which they were originally fortified to a second vial and extracted immediately. A third group of three samples was transferred just like the second but was subsequently set on the lab bench, capped but with approximately 10 mL headspace, for one half hour prior to extraction. The fourth group was first set for half an hour on the lab bench, capped but with approximately 10 mL headspace, then was transferred, recapped, and set for an additional half an hour prior to extraction.

**Extraction salt investigations**

In U.S. EPA method 551, NaCl is recommended as the extraction salt. An extraction salt is required as a means to increase the ionic strength of the aqueous matrix, thus increasing the extraction efficiency. Xie et al. (2,3) have found significant problems using NaCl as the extraction salt in the analysis of chlorinated water samples that have utilized ammonium chloride to reduce free chlorine. Chlorinated drinking water must be dechlorinated at the time of sampling as a means to eliminate additional reactions of free chlorine with humic and fulvic organic matter from the source water. Free chlorine is the general term used to define the equilibrium of hypochlorous acid (HOCl) and hypochlorite ion ($OCl^-$) introduced to the water as a result of chlorination. If free chlorine is not reduced at the time of sampling, additional DBPs will form in the sampling vial from these reactions, and the integrity of the sample at the time of sampling will not be preserved. Ammonium chloride is used as a reducing agent because it has no negative effects on any of the method analytes examined, specifically the haloacetonitriles, which are attacked by sodium sulfite or sodium thiosulfate. Ammonium chloride converts free chlorine to chloramine, which is much less reactive than free chlorine. At the time of extraction, when sodium chloride is added to the sample as the extraction salt, trace impurities of bromide ions ($Br^-$) can react with this combined chlorine species, and it is theorized that bromamines, which are believed to be more reactive than chloramines, are formed. These bromamines can, in turn, react with organic matter to potentially increase the amount of brominated organic DBPs (2).

To confirm this effect, a study was conducted investigating the extraction salts NaCl, $Na_2SO_4$, and $Br^-$-doped NaCl. These salts were used in the extraction of chlorinated tap water that had been preserved with ammonium chloride. The objective of this study was to compare the observed DBPs from samples that

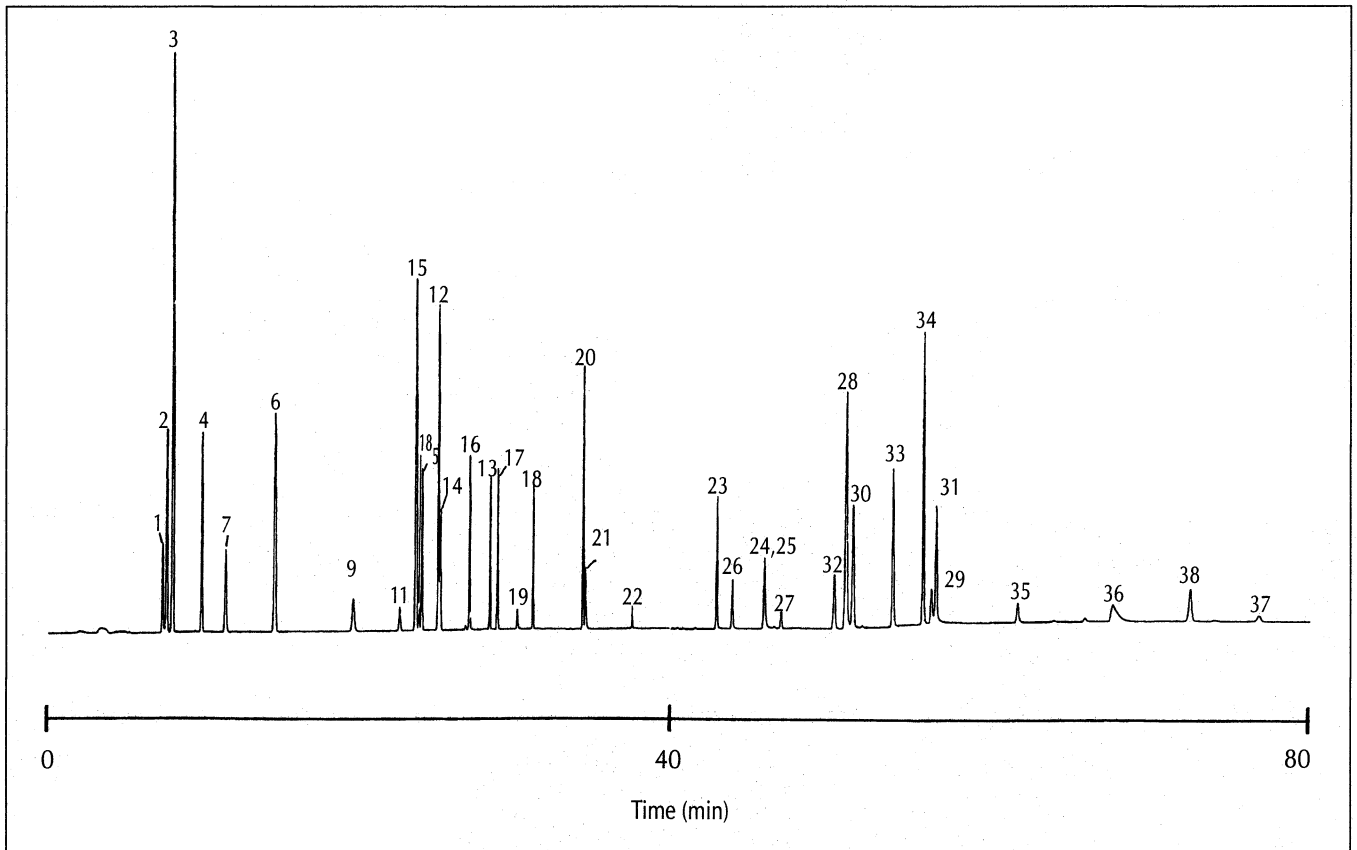


**Figure 2.** Analyte retention, confirmation Rtx-1301 column.

employed NaCl or $Na_2SO_4$ as the extraction salt. $Na_2SO_4$ was selected as an alternate extraction salt because $Br^-$ ions are much less likely to be present as a trace contaminant. In addition, the effect of delaying the sample extraction and dissolving the NaCl into the matrix prior to extraction was examined. By delaying the extraction, the $Br^-$ ions would have additional time to interact with combined chlorine and thus affect the brominated DBP results. This delayed extraction technique was also applied using NaCl that had been fortified with five times the maximum allowable trace $Br^-$ ions in American Chemical Society (ACS)-grade NaCl. ACS-grade NaCl is certified to contain less than 0.01% $Br^-$; therefore, the 10 g of NaCl added to 50 mL of sample could potentially contribute 1.0 mg $Br^-$. By adding 6.44 mg of NaBr (representing 5.0 mg of $Br^-$) to the 10 g of NaCl used for extraction, the effect of a fivefold increase over the maximum potential $Br^-$ present could be examined. This $Br^-$-fortified NaCl would definitively show any adverse effects as a result of trace $Br^-$ contamination in the NaCl extraction salt.

Using tap water that contained a residual free chlorine concentration of approximately 1 mg/L as the test matrix, triplicate samples were prepared and divided into four sample types. These sample types were characterized as shown in Table VII. Extractions were performed by first adding MtBE as the extraction solvent. The first and second types of samples that employed either 10 g NaCl or 12 g $Na_2SO_4$, respectively, were extracted immediately following the addition of the extraction salt. The third and fourth types of samples, incorporating

**Table V. Referenced Data for Figure 1**

Analyte peak identification and concentrations using MtBE for extraction of fortified reagent water on the primary column*

| Peak | Analyte | Concentration (µg/L) |
|---|---|---|
| 1 | Chloroform | 5.00 |
| 2 | 1,1,1-Trichloroethane | 5.00 |
| 3 | Carbon tetrachloride | 5.00 |
| 4 | Trichloroacetonitrile | 5.00 |
| 5 | Dichloroacetonitrile | 5.00 |
| 6 | Bromodichloromethane | 5.00 |
| 7 | Trichloroethylene | 5.00 |
| 8 | Chloral hydrate | 5.00 |
| 9 | 1,1-Dichloro-2-propanone | 5.00 |
| 10 | 1,1,2-Trichloroethane | 44.8 |
| 11 | Chloropicrin | 5.00 |
| 12 | Dibromochloromethane | 5.00 |
| 13 | Bromochloroacetonitrile | 5.00 |
| 14 | 1,2-Dibromoethane (EDB) | 5.00 |
| 15 | Tetrachloroethylene | 5.00 |
| 16 | 1,1,1-Trichloro-2-propanone | 5.00 |
| 17 | Bromoform | 5.00 |
| 18 | Dibromoacetonitrile | 5.00 |
| 19 | 1,2,3-Trichloropropane | 50.0 |
| 20 | 1,2-Dibromo-3-chloropropane (DBCP) | 5.00 |
| 21 | Surrogate: decafluorobiphenyl | 10.0 |
| 22 | Hexachlorocyclopentadiene | 28.0 |
| 23 | Trifluralin | 7.04 |
| 24 | Simazine | 200 |
| 25 | Atrazine | 200 |
| 26 | Hexachlorobenzene | 1.98 |
| 27 | Lindane (γ-BHC) | 30.1 |
| 28 | Metribuzin | 19.9 |
| 29 | Bromacil | 30.1 |
| 30 | Alachlor | 34.9 |
| 31 | Cyanazine | 60.4 |
| 32 | Heptachlor | 5.00 |
| 33 | Metolachlor | 70.0 |
| 34 | Heptachlor epoxide | 14.0 |
| 35 | Endrin | 5.00 |
| 36 | Endrin aldehyde | 7.00 |
| 37 | Endrin ketone | 4.96 |
| 38 | Methoxychlor | 20.1 |

* Bromofluorobenzene as the internal standard was not included in this chromatogram.

**Table VI. Referenced Data for Figure 2**

Analyte peak identification and concentrations using MtBE for extraction of fortified reagent water on the confirmation column*

| Peak | Analyte | Concentration (µg/L) |
|---|---|---|
| 1 | Chloroform | 5.00 |
| 2 | 1,1,1-Trichloroethane | 5.00 |
| 3 | Carbon tetrachloride | 5.00 |
| 4 | Trichloroacetonitrile | 5.00 |
| 5 | Trichloroethylene | 5.00 |
| 6 | Bromodichloromethane | 5.00 |
| 7 | 1,1-Dichloro-2-propanone | 5.00 |
| 8 | Chloropicrin | 5.00 |
| 9 | Tetrachloroethylene | 5.00 |
| 10 | 1,1,2-Trichloroethane | 44.8 |
| 11 | Dichloroacetonitrile | 5.00 |
| 12 | Dibromochloromethane | 5.00 |
| 13 | 1,2-Dibromoethane (EDB) | 5.00 |
| 14 | 1,1,1-Trichloro-2-propanone | 5.00 |
| 15 | Bromochloroacetonitrile | 5.00 |
| 16 | Bromoform | 5.00 |
| 17 | 1,2,3-Trichloropropane | 50.0 |
| 18 | Dibromoacetonitrile | 5.00 |
| 19 | 1,2-Dibromo-3-chloropropane (DBCP) | 5.00 |
| 20 | Surrogate: decafluorobiphenyl | 10.0 |
| 21 | Hexachlorocyclopentadiene | 28.0 |
| 22 | Trifluralin | 7.04 |
| 23 | Hexachlorobenzene | 1.98 |
| 24 | Atrazine/simazine | 400 |
| 25 | Lindane (gamma-BHC) | 30.1 |
| 26 | Heptachlor | 5.00 |
| 27 | Metribuzin | 19.9 |
| 28 | Alachlor | 34.9 |
| 29 | Metolachlor | 70.0 |
| 30 | Heptachlor epoxide | 14.0 |
| 31 | Bromacil | 30.1 |
| 32 | Cyanazine | 60.4 |
| 33 | Endrin | 5.00 |
| 34 | Endrin aldehyde | 7.00 |
| 35 | Methoxychlor | 20.1 |
| 36 | Endrin ketone | 4.96 |

* Bromofluorobenzene as the internal standard was not included in this chromatogram.

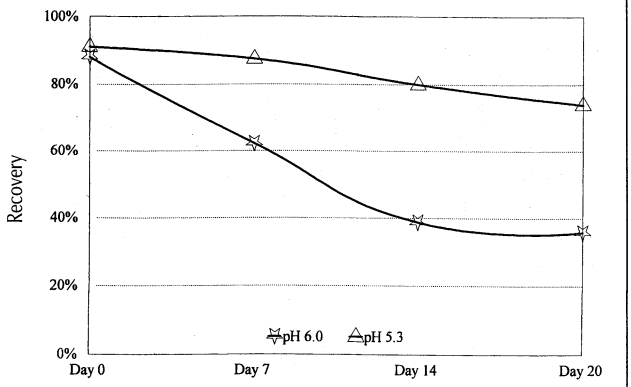


**Figure 3.** TCAN degradation (buffered reagent water).

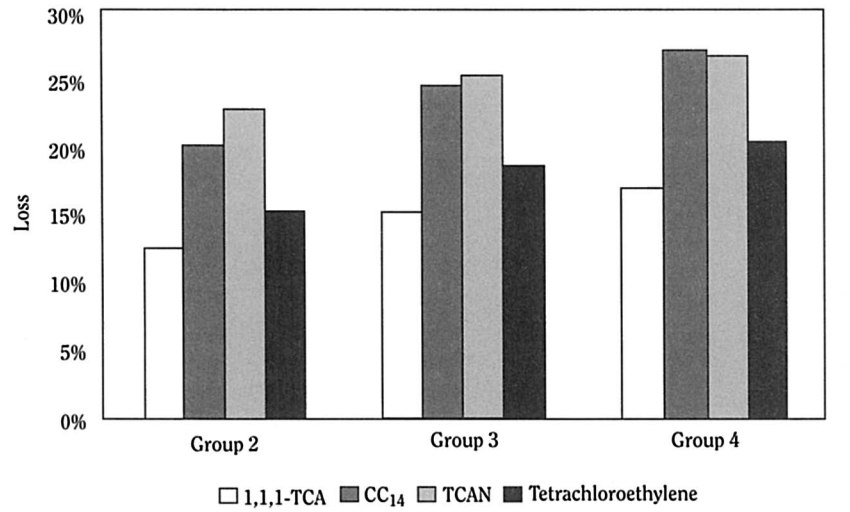


**Figure 4.** Volatility experiments. Effect of sample transfer and delayed extraction on %LOSS. %LOSS is expressed as the ratio of the decrease in concentration to the true value, multiplied by 100. Group 2, transferred only; group 3, transferred and set for half an hour; group 4, set for half an hour, then transferred, then set for half an hour.

delayed extraction, employed 10 g of either NaCl or $Br^-$-fortified NaCl, respectively. Following the addition of the MtBE extraction solvent and subsequent addition of either NaCl or $Br^-$-fortified NaCl as the extraction salt, delayed extraction samples were carefully rolled on the lab bench every 2 min to dissolve the salt. After 10 min, the extraction salt had completely dissolved, and after 15 min, the sample was extracted.

## Results and Discussion

### Analyte retention times and detection limits

Analyte retention times are listed for both the primary column and confirmation column in Table II. Analyte method detection limits (MDLs) and estimated detection limits (EDLs) are displayed in Tables III and IV for the primary and confirmation columns, respectively.

Chromatograms for the simultaneous primary and confirmation analysis of an extract from a fortified reagent water sample are shown in Figures 1 and 2 with reference data presented in Tables V and VI, respectively. The analyte concentrations shown in Tables V and VI vary greatly and reflect the attempt to normalize detector response for the various analytes in order to produce a uniform chromatogram.

### Matrix preservation and acidification

Following completion of the pH 5.3 stability study, recovery data were evaluated for analyte loss. When considering all the target compounds, TCAN is the most susceptible to base-catalyzed degradation. At pH 5.3, TCAN stability remained above 80% through 14 days, which was considered a substantial improvement when compared to the results obtained at the initial pH of 6.0, as shown in Figure 3.

At day 21, TCAN recoveries had fallen to 74% and 72% for reagent and tap water, respectively. Consequently, sample holding times were set at 14 days in method 551.1. All other method analytes were stable through 21 days at pH 5.3. Additionally, extract storage studies were conducted using the day 0 extracts. All analytes reflected recoveries between 80 and 120% when stored as extracts in a freezer held at –26°C for 21 days, but a conservative approach was adopted in the method, and a 14-day holding time for sample extracts was also defined.

Due to site-specific and seasonal variability of natural buffering in field samples, the dry phosphate buffer recommendation in U.S. EPA method 551.1 is 1.0 g of 1.0% $Na_2HPO_4$ and 99.0% $KH_2PO_4$ to 60 mL of sample. When 1.0 g of this dry phosphate buffer mixture is added to 60 mL of sample, the pH of nearly all drinking water matrices is reduced to between 4.8 and 5.5. This pH range is large enough to accommodate the various degrees of native buffering found in natural waters and yet is still low enough to ensure the stability of the haloacetonitriles.

### Sample handling and analyte volatility

Proper sample handling is essential when analyzing drinking water samples for volatile organic compounds. Following the analysis of the four groups of volatility experiment samples, the results indicate losses for all analytes from all three groups of transferred samples.

These losses were calculated as %LOSS in the following manner:

$$\%\text{LOSS} = \frac{(\text{concentration measured} - \text{control value})}{\text{control value}} \times 100$$

The "control value" was established from the initial set of nontransferred samples. Analyte %LOSS for the second group of samples averaged from –1.50 to –23.0%. The %LOSS values were more pronounced in the third group of samples, in which values ranged from –1.40 to –25.5%, and most dramatic in the fourth group, in which the lowest recoveries were observed and %LOSS ranged from –2.91 to –27.3%. Figure 4 illustrates these progressive volatility losses from groups 2–4 for 1,1,1-trichloroethane, carbontetrachloride, trichloroacetonitrile, and tetrachloroethylene, which were the four worst case analytes.

These results clearly indicate that samples should not be transferred from the original sampling vial in which they were shipped. The results also show the need to extract the sample immediately after reducing the sample volume to the 50 mL that is required for extraction. The best procedure for accurately reducing the sample volume to 50 mL is by using precalibrated sampling vials. Vials should be precalibrated in the laboratory before they are used for sampling by accurately measuring 50 mL of reagent water with a TD graduated cylinder, pouring this volume into the sampling vial, and scoring the vial at the meniscus. When a sample is received in the vial, the volume is reduced using a pipet to the precalibrated mark. If samples are received in 60-mL vials that have not been precalibrated, then 10 mL of sample should be removed, the remaining sample and vial should be weighed, and then, following sample extraction, the vial should be reweighed. The extracted sample volume is determined by the weight difference.

As an additional precaution to prevent volatile analyte losses, the extraction procedure of method 551 has been improved in method 551.1. Method 551 specifies that, after adding NaCl to the sample, the salt should be dissolved by "inverting and shaking the vial vigorously" prior to the addition of the extraction solvent methyl-*t*-butyl ether. It was believed that this could affect the analysis results, due to the high volatility of these method analytes. Therefore, method 551.1 has reversed these steps so that the extraction solvent is added prior to the addition of the extraction salt. Then, as the sample is extracted, the extraction salt dissolves. The extraction time has been extended to allow the salt sufficient time to dissolve, which enables the efficient extraction of all the method analytes.

**Table VII. Extraction Salt Comparison Study**

| Sample type | Description |
|---|---|
| 1 | 10 g NaCl as extracting salt with immediate MtBE extraction |
| 2 | 12 g $Na_2SO_4$ as extracting salt with immediate MtBE extraction |
| 3 | 10 g NaCl as extracting salt with delayed MtBE extraction |
| 4 | 10 g NaCl doped with $Br^-$ as extracting salt with delayed MtBE extraction; NaCl is fortified with 6.44 mg NaBr (5.0 mg $Br^-$) |

### Extraction salt investigations

By comparing the concentrations of brominated organic DBPs following the extraction and analysis of the various sample types displayed in Table VII, the effect of $Br^-$ in the extraction salt could be evaluated.

The results following these analyses are presented in Table VIII. The type-2 samples that employed $Na_2SO_4$ as the extraction salt had the lowest observed brominated organic DBPs. Slight increases of 12.6 and 6.9% for bromoform and dibromoacetonitrile, respectively, were measured in type-1 samples when compared to the type-2 samples. However, for the third

**Table VIII. Extraction Salt Comparison Study Analysis Results**

| | Type 1* | | Type 2* | | Type 3* | | Type 4* | |
|---|---|---|---|---|---|---|---|---|
| Analyte | Mean concentration (µg/L) | RSD (%) | Mean concentration (µg/L) | RSD (%) | Mean concentration (µg/L) | RSD (%) | Mean concentration (µg/L) | RSD (%) |
| Chloroform† | 68.7 | 1.62 | 62.4 | 2.50 | 68.5 | 2.06 | 69.4 | 0.22 |
| 1,1,1-Trichloroethane | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| Carbontetrachloride | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| Trichloroacetonitrile | 0.053 | 2.16 | 0.051 | 1.96 | 0.052 | 3.84 | 0.059 | 2.60 |
| Dichloroacetonitrile | 6.87 | 3.08 | 6.57 | 1.84 | 7.25 | 2.63 | 7.18 | 0.81 |
| Bromodichloromethane | 21.9 | 1.82 | 21.7 | 2.39 | 22.1 | 2.32 | 22.4 | 0.68 |
| Trichloroethylene | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| 1,1-Dichloro-2-propanone | 0.385 | 5.47 | 0.453 | 8.13 | 0.461 | 7.11 | 0.476 | 28.40 |
| Chloropicrin | 1.14 | 2.63 | 1.24 | 1.85 | 1.21 | 4.25 | 1.25 | 0.92 |
| Dibromochloromethane | 5.37 | 2.42 | 5.50 | 2.26 | 5.48 | 3.22 | 5.82 | 0.71 |
| Bromochloroacetonitrile | 2.50 | 4.21 | 2.39 | 1.58 | 2.79 | 4.13 | 2.85 | 1.60 |
| 1,2-Dibromoethane | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| Tetrachloroethylene | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| 1,1,1-Trichloro-2-propanone | 4.05 | 2.24 | 3.92 | 0.96 | 4.09 | 2.72 | 4.05 | 1.40 |
| Bromoform | 0.493 | 4.17 | 0.438 | 1.97 | 0.494 | 4.04 | 1.07 | 8.48 |
| Dibromoacetonitrile | 0.449 | 2.28 | 0.420 | 0.72 | 0.734 | 7.33 | 1.97 | 3.55 |
| 1,2-Dibromo-3-chloropropane | < 0.05 | – | < 0.05 | – | < 0.05 | – | < 0.05 | – |
| Surrogate recovery (%) Decafluorobiphenyl | 108 | 1.418 | 102 | 0.98 | 111 | 1.80 | 117 | 3.22 |

* Mean and RSD calculated from triplicate analysis.
† Chloroform concentration was beyond the highest calibration point of 50 µg/L, but dilutions were not analyzed because the primary focus of the experiments was to monitor the brominated DBP concentrations.

type of samples, in which NaCl was allowed to dissolve and the extraction was delayed, bromoform and dibromoacetonitrile concentrations increased by 12.8 and 74.8%, respectively, over what was observed in the type-2 $Na_2SO_4$ samples. Type 4 samples, for which $Br^-$ was intentionally fortified into the NaCl and extraction was delayed, displayed the most dramatic brominated DBP increases over the type-2 $Na_2SO_4$ samples; bromoform and dibromoacetonitrile increased 144 and 369%, respectively.

These findings support the arguments of Xie and confirm the potential for increased concentrations of brominated organic DBPs when NaCl is used as the extraction salt in ammonium-chloride-quenched samples. As a result, the use of $Na_2SO_4$ as the extraction salt is recommended in method 551.1.

### Additional changes in U.S. EPA 551.1

To insure the proper performance of the GC system that is used to analyze samples, a Laboratory Performance Check solution (LPC) has been included in method 551.1. This check solution is designed to monitor instrument performance based on the parameters of instrument sensitivity, chromatographic performance, column performance, and breakdown of endrin. These parameters are listed in Table IX along with the method analytes utilized to perform this evaluation, their concentration in MTBE or pentane, and the acceptance criteria. If endrin breakdown exceeds 20%, the problem can most likely be solved by performing routine maintenance on the injection port, including replacing the injection port sleeve and all associated seals and septa. If column or chromatographic performance criteria cannot be met, new columns may need to be installed, column flows may need to be corrected, or modifications may need to be adapted to the oven temperature program. During early method development work, significant chromatographic and column performance problems were observed while using a DB-1 column that had been used for several years in drinking water extract analysis. By installing a new DB-1 column, these performance problems were overcome. If the columns to be used for method 551.1 have been used for several years or have had extended use with extracts from harsh sample matrices (e.g., wastewater, acidified sample extracts, hazardous waste samples), it may be difficult to meet the criteria established for this LPC standard, and column replacement may be the best alternative. If a laboratory is not conducting analyses for pesticides and herbicides, a modified LPC solution may be prepared. This modified LPC solution can omit the endrin analyte breakdown component as well as the resolution requirement for bromacil and alachlor under column performance. In addition, substitute analytes in place of lindane for the sensitivity check and hexachlorocyclopentadiene for chromatographic performance can be selected. These substitute compounds must meet the same acceptance criteria as listed in Table IX with a concentration for the substitute sensitivity check analyte near the minimum detection limit for that analyte and the concentration for the substitute chromatographic performance analyte at a middle- to high-calibration level.

In addition, due to concerns over the safety of MtBE as the extraction solvent, method 551.1 has specified pentane as an alternate solvent. This solvent does not extract chloral hydrate from aqueous samples and therefore cannot be used if chloral hydrate analysis is required. Also, 5.0 mL of pentane rather than 3.0 mL of MtBE is used for extraction. This larger volume is required as a means to increase the ratio of pentane to water. This was required because pentane does not emulsify into the water as efficiently as MtBE. In addition, due to the high volatility of pentane, an internal standard must be used with this extraction solvent. Bromofluorobenzene is recommended, due to the fact that it is highly unlikely to be observed in any field samples.

Finally, method 551 specified an extracted sample size of 35 mL collected in 40-mL vials and a 2.0-mL volume of MtBE

**Table IX. Laboratory Performance Check Solution**

| Parameter | Analyte | Concentration (µg/mL) in MtBE or pentane | Acceptance criteria |
|---|---|---|---|
| Instrument sensitivity | Lindane (γ-BHC) | 0.000200 | Detection of analyte; signal-to-noise > 3 |
| Chromatographic performance | Hexachlorocyclopentadiene | 0.0200 | PGF between 0.80 and 1.15* |
| Column performance | Bromodichloromethane | 0.0300 | Resolution > 0.50† |
| | Trichloroethylene | 0.0300 | |
| | Bromacil | 0.0830 | Resolution > 0.50 |
| | Alachlor | 0.0830 | |
| Analyte breakdown | Endrin | 0.0300 | % BD < 20%‡ |

* PGF = Peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W_{(1/2)}}{W_{(1/10)}}$$

where $W_{(1/2)}$ is the peak width at half height, and $W_{(1/10)}$ is the peak width at one tenth height.

† Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where $t$ is the difference in retention times between the two peaks, and $W$ is the average peak width, at the baseline, of the two peaks.

‡ % BD = Percent breakdown. Endrin breakdown calculated using the equation.

$$\%\ BD = \frac{\text{(endrin ketone area + endrin aldehyde area)}}{\text{(endrin ketone area + endrin aldehyde area) + endrin area}} \times 100$$

extraction solvent. Often there was insufficient space in the 40-mL sampling vial to add the required 8 g of NaCl and 2.0 mL of MtBE once 5.0 mL of aqueous sample was removed. In addition, with this small volume of solvent, it was difficult to fill two autosampler vials with the 1.5 mL of solvent that remained after sample extraction. Only 1.5 mL of solvent can be recovered from the extracted sample because a thin layer of extraction solvent remains at the solvent–aqueous layer interface, and MtBE exhibits a small degree of water solubility. Consequently, the volume of sample to be extracted was increased to 50 mL following collection in a 60 mL vial. This 60-mL vial allowed for approximately 10 mL of headspace, which permitted sufficient room for the 20 g of $Na_2SO_4$ specified in method 551.1 as the extraction salt as well as 3.0 mL of MtBE for extraction or 5.0 mL of pentane as the alternate extraction solvent. The larger volume of extraction solvent makes it much easier to fill a duplicate autosampler vial. This duplicate vial can serve as a backup sample in the event of an instrument malfunction or can be used to perform a separate confirmation analysis if simultaneous confirmation cannot be performed.

## Conclusion

Several changes have been incorporated into U.S. EPA method 551.1 that significantly improve the procedure over method 551. By expanding the analyte list to include halogenated pesticides and herbicides, the scope of the method has been widened. Flexibility has been built into the method in several ways. For instance, even though the analyte list has expanded, laboratories are not required to perform analysis for the total analyte list if their project requirements include only select analytes. In addition, a laboratory may choose to use pentane as the extraction solvent over MtBE if chloral hydrate analysis is not required. A potential problem with NaCl as the extraction salt has been overcome through the use of $Na_2SO_4$ as the extraction salt. Analyte volatility has been addressed and precautions to avoid analyte losses have been specified.

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Manuscript accepted November 19, 1996.