

AQR Color-Tec[®] Method

Soil/Water Analysis Procedure for Detection of Total Chlorinated Volatile Organic Halocarbons



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AQR Color-Tec[®] Method

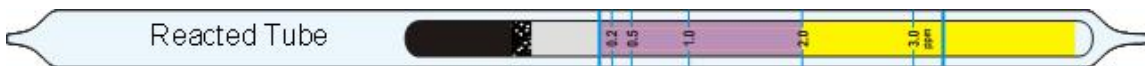
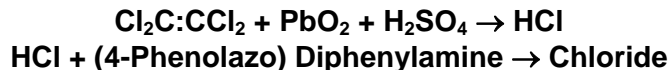
Soil/Water Analysis Procedure for Detection of Total Chlorinated Volatile Organic Halocarbons

Important: Read all instructions, procedural guidelines, and safety precautions for all components included in this kit before implementing the AQR Color-Tec[®] method.

1.0 Introduction (Method Principle)

AQR Color-Tec[®] is a field-based analytical method which combines the use of colorimetric gas detector tubes (originally designed for occupational breathing-zone monitoring) with sample purging to detect very low (*to* <2µg/L) concentrations of chlorinated volatile organic halocarbons (CVOHs) in liquid and solid samples. The AQR Color-Tec[®] method provides fast, low-level, economical, decision-quality data which maximizes sampling frequency and sample coverage to locate source zones and delineate dissolve-phase contaminant plumes.

Samples are analyzed by using a hand-operated vacuum pump to purge the volatile compounds from a groundwater or soil sample through the colorimetric tube, which is designed to produce a distinct color change when exposed to chlorinated compounds. The colorimetric tubes and hand pumps used for the AQR Color-Tec[®] method are manufactured by Gastec[®], Inc. Each colorimetric tube contains an oxidizer (PbO₂) and a catalyst (H₂SO₄) which decomposes and converts the chlorinated compounds to hydrogen chloride, which discolors a reagent (4-phenylazodiphenylamine) in the tube from yellow to purple. The reaction formula provided by Gastec[®] for the PCE tube is as follows:



The colorimetric tubes react positively to all chlorinated volatile organic halocarbons, including saturated and unsaturated chlorinated alkenes and alkanes. Therefore, the total response indicated by the detector tube reflects the sum of the concentration of each individual chlorinated compound present in the sample. In comparisons of the colorimetric tube readings to the pre-prepared standards, the method routinely detects these compounds at concentrations of 2 microgram per liter (µg/L) of total CVOCs and below. In comparisons using the field-generated data, the AQR Color-Tec[®] method routinely detects total chlorinated compounds below the regulatory clean-up levels of the specific chlorinated compounds detected by gas chromatograph/mass spectrometer (GC/MS) analysis in split samples. When used in accordance with AQR Color-Tec[®] method procedures, the method can detect total chlorinated compounds in water

samples at concentrations at or below the quantitation limit of EPA Method 8260 using GC/MS techniques. Detection of concentrations below 1 µg/L are common.

The AQR Color-Tec[®] method is primarily qualitative (detects the presence/absence of a compound or class of compounds). The colorimetric gas detector tubes used in the AQR Color-Tec[®] method are designed to detect CVOHs in ambient air. Color-Tec[®] method is an alternate use of these tubes, which involves purging CVOHs from a water or soil sample and concentrating them through the colorimetric tube to evoke a color change when any CVOHs are present in the sample at sufficient concentrations to be detected.

When the colorimetric tubes are used in the AQR Color-Tec[®] method, the units (ppmV) printed on the tubes have no direct relationship to the quantity of CVOHs dissolved in the water sample which is being analyzed. The distance that the color change travels through a tube (the tube reading) is a relative response to the amount of chlorinated-compound molecules that have been purged from the sample and directed into the tube. Therefore, the units printed on the tubes are used only to record the relative response for each analysis in order to facilitate comparison of the response to other sample results or for comparison to laboratory GC/MS methods. The relative response must not be considered a concentration in ppmv (as printed on the tubes), but rather as “relative response units” which must be compared to known values in order to yield an estimate of the actual concentration present in the sample.

Although Color-Tec[®] does not provide a specific measurement that directly relates to the concentrations in the sample, the level of intensity of a positive colorimetric tube reaction (the relative response) does provide an indication of the magnitude of the concentration. Tube readings may be used to estimate the concentration of CVOHs present in the sample by comparing Color-Tec[®] results to the results of split samples analyzed by GC/MS. It is customary to select from 5 to 20 percent of the samples in a data set for comparison analysis. Given a sufficient quantity of split sample pairs and sufficient range of concentration values, the GC/MS-to-Color-Tec[®] comparison data may be used to obtain estimated concentrations for samples in the data set which were analyzed only using the AQR Color-Tec[®] method. This can be achieved using linear regression analysis of the comparison data. Statistical analysis of the comparison data can also be performed to determine confidence of the Color-Tec[®] zero values, essentially providing a Color-Tec[®] method detection limit (MDL) for the data set. This is discussed in further detail below in Sections 9 and 10.

The Gastec[®] 133-series colorimetric tubes used with the AQR Color-Tec[®] method, are capable of detecting all chlorinated volatile organic halocarbons at concentrations at or below the EPA Maximum Contaminant Levels (MCL) of any individual compound in that class of compounds. Although Color-Tec[®] does not identify the specific chlorinated compound in the sample, or yield a specific value related to the concentration in the water or soil sample, the level of intensity of each positive tube reaction provides the general magnitude of the concentration in the sample; such as “very low” (at or below EPA MCLs), “low” (likely above EPA MCLs), “medium” (likely at a concentration in the hundreds of µg/L), and “high” (likely at a concentration in the thousands of µg/L). These capabilities combined with low per-sample cost and speed make the AQR Color-Tec[®] method a highly effective tool for field-based decision-making at chlorinated solvent sites.

2.0 AQR Color-Tec[®] Test Kit Parts Description

The AQR Color-Tec[®] Chlorinated VOH Soil/Water Test Kit System consists of three primary components:

1. Hardware Kit - Contains reusable equipment and carrying case;
2. 20-Sample Expendables Kit - Contains components needed for analysis of 20 water or soil samples (available for low, medium, or high range detection of total CVOHs);
3. QA/QC Kit – Contains components needed to perform suggested QA/QC procedures to insure method performance and provide method confidence

2.1 Materials Provided

2.1.1 Hardware KIT (See Figure 1)

Item	Quantity
RAE [®] Piston pump	1
AQR Color-Tec [®] Pump Stand	1
Corning [®] Hot Plate	1
Stainless Steel Heating Pan	1
Nalgene [®] VOA Heating Rack	1
Thermometer	1
Decontamination Syringe	1

2.1.2 20-Sample Expendables Kit (analyzes 20 water or soil samples) (See Figure 2)

Item	Quantity
Low-Range (133LL) Colorimetric Detector Tubes	21
300µg/L-TCE reference standard in flame-sealed ampoule	1
10 ml Pipette (for transferring standard)	3
40 Milliliter VOA Vial (filled with water for spike)	1
Medium-Range (133L) Colorimetric Detector Tubes	2
High-Range (133M) Colorimetric Detector Tubes	1
Extraction Needle Assemblies	24
40 Milliliter VOA Vials – empty (for samples)	40
40 Milliliter VOA Vial – no cap (for heating tubes)	1
Carbon Filter	2
Carbon Filter Luer Assembly	2
Purge Needle	2
Nitrile Safety Gloves (pair)	1

2.1.3 QA/QC Kit (See Figure 3)

Item	Quantity
Low-Range (133LL) Colorimetric Detector Tubes	5
Toluene colorimetric Detector Tube	1
60µg/L-TCE reference standard in flame-sealed ampoule	2
300µg/L-TCE reference standard in flame-sealed ampoule	1
600µg/L-TCE reference standard in flame-sealed ampoule	1
10 ml Pipette (for transferring standards)	4
40 ml VOA Vials (empty – (for toluene test samples)	2
40 ml VOA Vials (pre-filled with organic-free water)	4
Extraction Needle Assemblies	5
Purge Needle	1
Carbon Filter	1
Carbon Filter Luer Assembly	1
Nitrile Safety Gloves (pair)	1

Figure 1
AQR Color-Tec[®] Materials Provided in Hardware Kit



Figure 2
AQR Color-Tec[®] Materials Provided in
20-Sample Expendables Pack

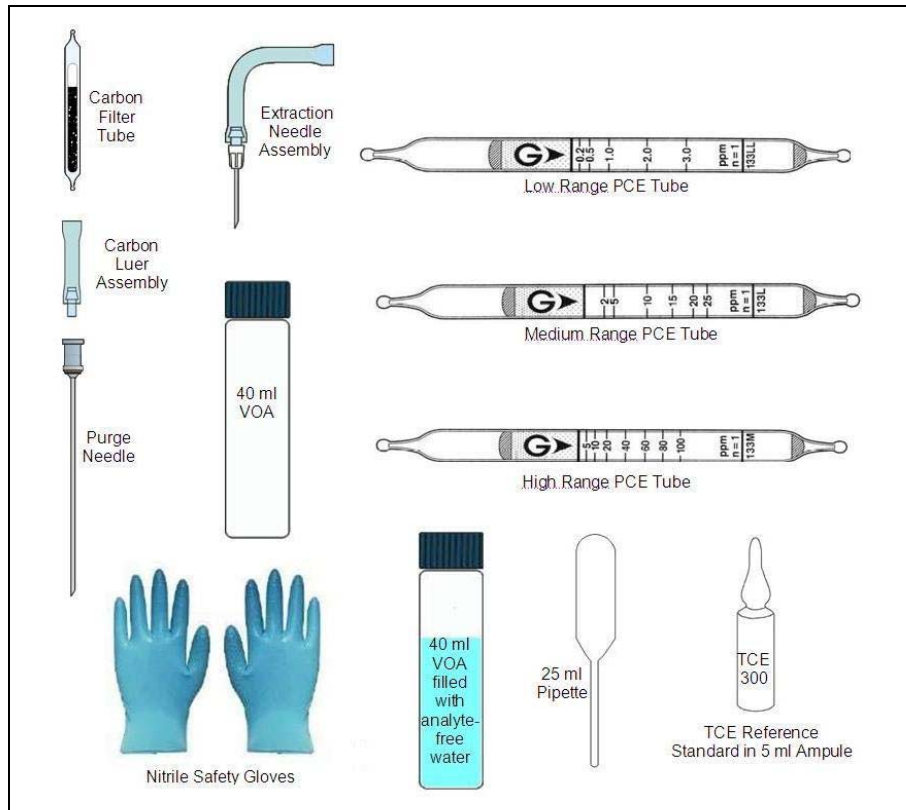
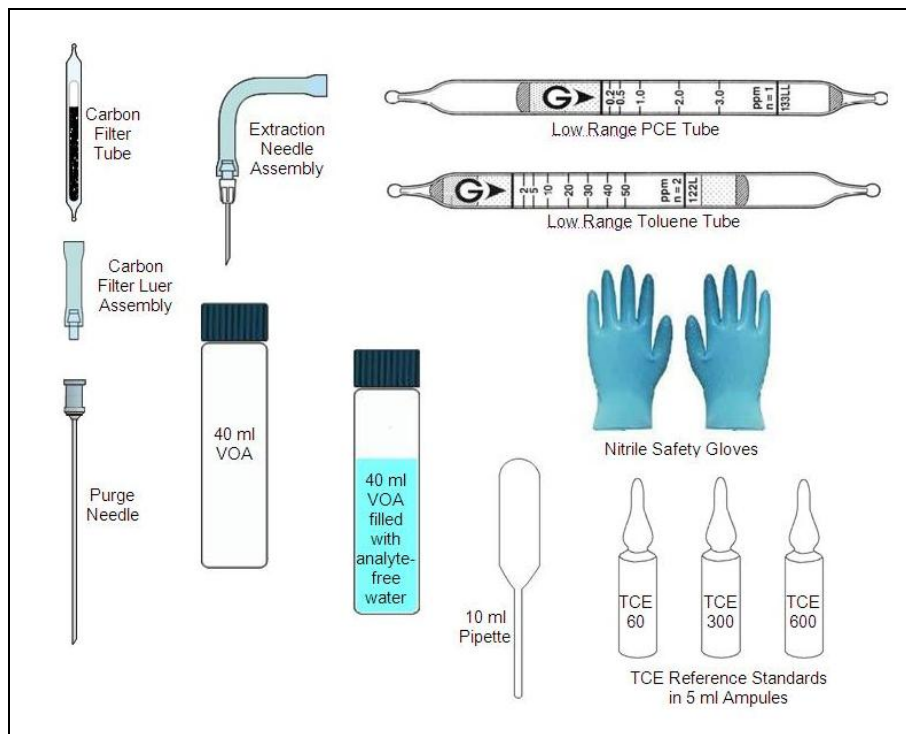


Figure 3
AQR Color-Tec[®] Materials Provided in QA/QC Test Pack



2.2 Accessories Supplied by User

The following items (not provided in the AQR Color-Tec[®] kit) are suggested for use with the AQR Color-Tec[®] method to perform the listed functions.

Item	Purpose
Organic-free water	For soil sample extraction and equipment decontamination
Safety gloves	Personal protection
Safety glasses	Personal protection
120V AC power source	For hot plate
Permanent marker	Labeling sample bottles
40 Milliliter VOA Vials	For split samples to be analyzed by laboratory methods

The VOA vials used to perform the AQR Color-Tec[®] method are provided in each kit (two vials per sample). The user may wish to collect a quantity of split samples for laboratory analysis to provide comparison data which may be used to determine site-specific method detection limits and/or to tentatively quantify AQR Color-Tec[®] results.

2.3 Storage & Stability of Colorimetric Tubes and Reference Standard Ampoules

The Gastec colorimetric tubes have a shelf-life of two years with refrigeration. Tubes should be stored at or below a temperature of 10°C/50°F when not in use. Colorimetric detector tubes are single-use (one tube per analysis) and should be used immediately after the tips are broken. Tube readings should be recorded immediately following analysis because the intensity of the color-change fades over time. Each box of tubes has an expiration date printed in red ink on the top of each box. When heating the tubes for use with the AQR Color-Tec[®] method, it is recommended that the tube temperature does not exceed 40°C/104° F.

Other procedures and guidelines for use of the colorimetric tubes with the AQR Color-Tec[®] method are presented in this manual. Other procedures and guidelines associated with the use of the tubes for their designed purpose (gas detection in ambient air) are included in the tube manufactures data sheets and tube instructions included in the tube packaging.

The QA/QC reference standards are provided in 5ml flame sealed ampoules to prevent loss of volatiles and generally have a shelf life of one year with refrigeration.

2.4 Field Preparation of QA/QC Standards

Each 20-sample AQR Color-Tec[®] expendables kit is equipped with a TCE reference standard and a VOA vial pre-filled with analyte-free water used to prepare a 10 µg/L spiked sample. AQR Color-Tec[®] QA/QC kits are equipped with supplies to perform a variety of QA/QC tests including TCE reference standards and three VOA vials pre-filled with analyte-free water used to prepare 10 µg/L, 50 µg/L, and 100 µg/L spiked samples. The QA/QC reference standards are provided in 5ml, flame sealed glass ampoules labeled TCE-60, TCE-300, and TCE-600. These reference standards are used to prepare sample spikes for field QA/QC testing by transferring the contents of each

ampoule into each of three VOA vials pre-filled with analyte-free water. After transferring the reference standards in the ampoules to the VOA vials pre-filled with analyte-free water, these VOAs will contain TCE concentrations of 10 µg/L (green label), 50 µg/L (yellow label), and 100 µg/L (red label). These spiked samples are then analyzed using the AQR Color-Tec® method to analytical confidence. Spiked control samples are used to insure that the method is detecting the target compounds within reasonable limits and to provide a basis for estimating concentrations based on the AQR Color-Tec® responses.

3.0 Sample Collection and Preparation

3.1 Liquid Sample Media

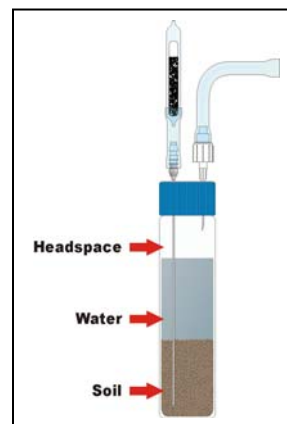
Collect the water or other liquid sample media directly from your sampling device into two 40 ml VOA vials by filling each vial to ~70% capacity (i.e. to about 1-inch below the shoulder of each vial). *Note: The second vial serves as a duplicate sample which may be needed later during the AQR Color-Tec® analysis process.* Tightly secure the caps onto the partially-filled VOA vials.

IMPORTANT NOTE: The VOA vials containing the liquid sample to be tested must contain an air-filled headspace to accommodate purging. The caps must be tightened sufficiently to prevent loss of CVOHs during the time between sample collection and analysis (which includes the heating process) and to prevent air leakage during the purging process.

3.2 Solid Sample Media

Place about 1.5 inches of your soil (or other solid sample media) into the bottom of each of two VOA vials (i.e. approximately 30 grams in each vial). *The second vial serves as a duplicate sample which may be needed later during the analysis process.*

Immediately after inserting the soil (or other solid sample media) into the two vials, add organic-free or other “clean” water to each VOA vial until they are both ~70 % full (i.e. to approximately 1-inch below the shoulder of each vial). Tightly secure the caps onto the partially-filled VOA vials. Once the caps are secure, shake the VOA vials vigorously for approximately for 5 to 10 seconds to thoroughly mix the soil and water. Additional mixing may be necessary for soil matrices comprised of clay-sized particles. The purpose of the mixing is to transfer any chlorinated compounds suspended in the soil matrix to the water to facilitate more effective purging.



IMPORTANT NOTE: The VOA vials containing the solid sample media and “clean” water must contain an air-filled headspace to accommodate purging. The caps must be tightened sufficiently to prevent loss of CVOHs during the time between sample collection and analysis (which includes the heating process) and to prevent air leakage during the purging process.

3.3 Purpose of Duplicate Samples

The AQR Color-Tec® method is designed for use with two VOA vials (an original and a duplicate) for each sample collected. In certain situations, the duplicate sample may not be used in the performance of the method. However, the duplicate sample should always be collected in the event that it is needed to complete the analysis process. The duplicate sample may be used in either of the following situations:

- When the initial test does not induce a color change in the colorimetric tube, the second VOA vial containing the duplicate sample, may be purged (using the same colorimetric tube) to increase the probability of detecting very low (< 10 µg/L) concentrations.
- When the initial test induces a color change that exceeds the upper limit of the LL tube (a tube reading > 3), the extra VOA vial can be used to analyze the sample using higher range colorimetric tubes (133L or 133M) to tentatively quantify the higher concentration of chlorinated compounds in the sample.

3.4 Collection of Split Samples for Laboratory Analysis

It is recommended that sample splits be collected for laboratory comparison analysis from 5 to 20 percent of the total quantity of samples analyzed using the AQR Color-Tec[®] method. Given a sufficient quantity of split sample pairs and sufficient range of concentration values, the GC/MS-to-AQR Color-Tec[®] comparison data may be used to obtain estimated concentrations for samples in the data set which were analyzed only using the AQR Color-Tec[®] method. This can be achieved using linear regression analysis of the comparison data. Statistical analysis of the comparison data can also be performed to determine site-specific AQR Color-Tec[®] method performance data. This is discussed in further detail below in Sections 9 and 10.

4.0 Heating Colorimetric Tubes and Samples

The colorimetric gas detector tubes used in the AQR Color-Tec[®] method were designed solely for the purpose of detecting volatile organic compounds (CVOHs) in ambient air. When using the tubes for CVOH detection in **ambient air**, the calibrated operating temperature is 20°C/68°F, and the value obtained from the tube in (ppmV) is the actual concentration of CVOHs present in the **ambient air** being tested. Using the tubes at temperatures above or below 20°C/68°F, for the purpose of testing **ambient air**, introduces error into the measurements, thus a correction factor must be applied to correct that error. The temperature correction factors for using the colorimetric tubes for the purpose of analyzing **ambient air** are as follows:

Table 1
Correction Factors for Ambient Air Analysis Using Colorimetric Tubes

Temperature ° C	0°	10°	20°	30°	40°
Temperature ° F	32°	50°	68°	86°	104°
Ambient Air Correction Factor	2	1.3	1	0.7	0.55

Because the AQR Color-Tec[®] method is an alternate use of the colorimetric tubes which involves purging and concentrating CVOHs from water or soil samples into the tubes, the units (ppmV) printed on the tubes have no direct relationship to the quantity of CVOHs dissolved in the water/soil sample which is being analyzed (i.e. the magnitude of the color change in the tube represents only a relative response to the concentration of CVOHs present in the water/soil sample). Thus, the temperature corrections discussed above and shown in Table 5 are not used when using the colorimetric tubes as part of the AQR Color-Tec[®] method.

Since the colorimetric tubes are more sensitive to the presence of chlorinated compounds at 40°C/104°F, and the purpose of the AQR Color-Tec[®] method is to detect the presence/absence of CVOHs in water at concentrations at the lowest concentrations possible, it is strongly recommended that the tubes be heated to their optimum sensitivity (40°C/104°F) and that the samples should also be heated to maximize the transfer of CVOHs from the water sample to the colorimetric tube.

To heat the samples and colorimetric tubes, connect the hot plate to a United States standard 120V AC power source and switch it on by turning the thermostat to a setting of between 4 and 5 (refer the hot plate manufacturer's manual for complete operating instructions). Place the test tube rack into the steel pan, fill the pan $\frac{3}{4}$ full of water and place the pan onto the hot plate. Remove the cap from a 40 ml VOA, fill it with clean water, and place it in the test tube rack. Place several un-broken colorimetric tubes into the water-filled VOA for heating. Place the thermometer into the water-filled VOA with the colorimetric tubes. Adjust the hot plate control knob periodically to maintain a water temperature of approximately 40°C/104°F. The samples and colorimetric tubes should not be heated in excess of 40°C/104°F. Special attention must be paid to the temperature of the water to avoid prolonged overheating the samples and tubes.

Given the size of the heating pan and VOA rack, generally only 3 sets of samples are heated at the same time. When a pair of VOAs is removed from the heating rack and placed on the pump stand, it can be replaced with a new pair for heating. After collection, samples should remain in a cool place until ready to be heated and analyzed. It is recommended to avoid heating the samples for more than about 5 minutes to avoid loss of CVOCs.

5.0 Sample Purge and Analysis Procedure

Break both glass tips of a 133LL colorimetric tube.

Attach the 133LL colorimetric tube to an extraction needle assembly by inserting the clear end of the glass tube into the open end of the clear tubing.

Insert the yellow end of the colorimetric tube into the tip of the RAE piston pump. For complete piston pump operation instructions please refer to the RAE[®] Piston pump manual included in the AQR Color-Tec[®] hardware kit.

Place both tightly-capped VOA vials containing the pre-heated water sample into the two bottle holders on the pump stand (see Figure 2).

Insert the extraction needle (the short needle attached to vinyl tubing) into the septa of the VOA vial. Be sure that the tip of the extraction needle is positioned within the headspace of the VOA vial (above the water level). Note: Do not insert the extraction needle as far as it will go into the headspace of the VOA vial, but rather only insert it to a point slightly beneath the inside of the septa to reduce the possibility of sample water entering the extraction needle assembly and colorimetric tube during the purging process.

Insert a purge needle (the 4-inch needle) into the septa of the VOA vial, and push the tip of the purge needle into the water sample to the bottom of the VOA vial.

Attach a carbon filter and carbon luer assembly to the luer fitting on the top of the purge needle (See Figure 2). Section 6 below further describes the carbon filter assembly set-up procedure.

Pull pump handle out and lock in place at the 50cc position. *Note: For complete piston-pump operation instructions please refer to the RAE[®] Piston pump manual included in the AQR Color-Tec[®] Hardware Kit.*

Observe the sample in the VOA vial to determine if air bubbles are flowing from the tip of the purge (long) needle through the sample. Air should be flowing (bubbling) through the sample. If air is not flowing through the sample, one of the following problems may have occurred:

- Clogged/blocked purge (long) needle;
- Clogged/blocked extraction (short) needle;
- Colorimetric tube is not securely connected to hand pump;
- Colorimetric tube is not securely connected to extraction needle tubing;
- VOA cap is not tightly sealed;
- Broken/bad seal in hand pump.

Note: A complete troubleshooting guide with causes and solutions to these and other potential problems is presented as Table 6 of this manual.

When the pump handle is locked open at the 100cc position, purging should continue through the sample for approximately 60 seconds. If the 100cc purge cycle ends (bubbling stops) before approximately 60 seconds have elapsed, the pump may require servicing (see the RAE[®] pump manual for pump operation and servicing instructions).

6.0 Carbon Pre-Filter

Because ambient air is used to purge the samples, a carbon pre-filter is provided for attachment to the purge needle to prevent possible airborne contaminants from passing through the sample and entering the detector tube during the purging process. To use the carbon pre-filter, break both tips of a carbon filter tube and insert the end of the tube onto the carbon lure assembly (make sure the air-flow arrows on the carbon tube point toward the carbon lure assembly), then tightly insert the male lure fitting on the carbon lure assembly into the female lure fitting on the purge needle (see Figure 2). At sites where little or no ambient air contamination is present, a single pre-filter tube may be reused for several days. However, at sites where high concentrations of airborne chlorinated compounds are suspected or have been confirmed in the ambient air, the pre-filter tubes may need to be replaced more frequently. For most situations, one carbon filter per 20 samples is more than sufficient (the AQR Color-Tec 20-sample Expendables Kit contains 2 carbon pre-filters).

7.0 Sample Purging and Detection Methodology

Samples may be purged using 50 cubic centimeters (cc), 100cc, or 200cc purge volumes. These various purge volumes are used in succession to maximize the low-level detection capability and detection range of each tube, thereby reducing the number of tubes needed to tentatively quantify the concentration of total chlorinated compounds

in the sample. The pump stand is equipped with two VOA-vial holders to accommodate a second (duplicate) sample to be collected from each sampling location. This duplicate sample (collected and prepared in the same manner as the original sample) serves the following two potential purposes:

1. When purging the initial VOA vial does not induce a color change in the colorimetric tube, the second VOA vial containing the duplicate sample, may be purged (using the same colorimetric tube) to increase the probability of detecting very low (< 10 µg/L) concentrations.
2. When the initial test induces a color change that exceeds the upper limit of the LL tube (a tube reading > 3), the extra VOA vial can be used to analyze the sample using higher range colorimetric tubes (133L or 133M) to tentatively quantify the higher concentration of chlorinated compounds in the sample.

7.1 50cc Purge Volume

Initially, all samples are analyzed using a Gastec® 133-LL tube with a 50cc purge cycle. If the 50cc purge induces a color change reading of 1.5 to 3.0, read the calibration scale value aligned with the stained/unstained interface in the tube and use the pump stroke correction factors provided on the colorimetric tube instruction sheets to determine the correct reading for a 50cc purge volume. If the concentration in the sample exceeds the upper detection limit of the tube (i.e. the color change moves beyond the upper limit of the calibration scale printed on the tube), repeat the analysis using duplicate samples and higher range tubes (133-L and 133-M) until the color change reaction stops within the calibration scale on the tube. If the color change reaction exceeds the upper limit of the calibration scale of the M tube, the sample contains a concentration of chlorinated compounds above the upper detection capability of the AQR Color-Tec® Method.

7.2 100cc Purge Volume

Following completion of the 50cc purge cycle, if the concentration in the sample has induced a color change in the tube which traveled less than half the distance of the calibrated portion of the reagent phase of the tube, pull the pump handle outward and lock it into the 100cc position to complete a full purge cycle. Record the value aligned with the stained/unstained interface on the tube. No correction factor is needed for a 100cc purge.

7.3 200cc Purge Volume

Following completion of the 100cc purge cycle, if the concentration in the sample has induced only a very slight (<0.5) color change reaction or no color change reaction, remove the purge needle and extraction needle assembly from the VOA vial containing the original sample and insert them into the VOA vial containing the duplicate sample (which has also been pre-heating) and repeat the 100cc purge cycle using the same colorimetric tube.

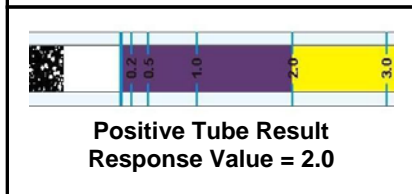
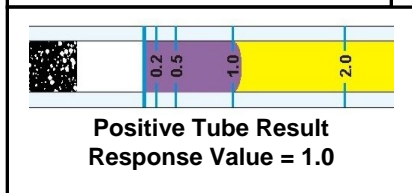
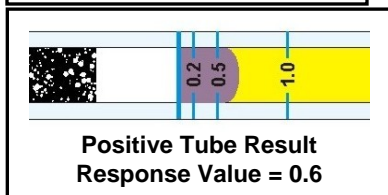
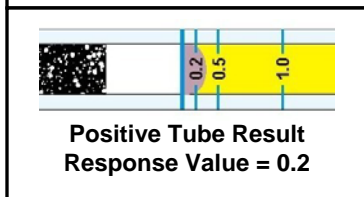
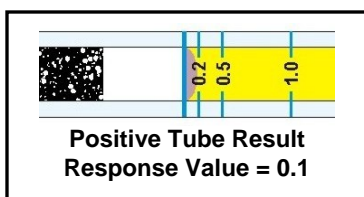
Note: When purging the duplicate sample using a second 100cc purge cycle is necessary, remove both needles from the original VOA vial. With the extraction needle tubing remaining attached to the colorimetric tube, remove both needles from the original VOA vial and immediately insert both needles into the septa of the duplicate sample VOA vial. Before re-inserting the pump handle, temporarily remove the colorimetric tube from the tip of the hand pump and re-insert the pump handle completely into the pump while the tube is un-attached. Re-attach the colorimetric tube into the pump tip and pull the pump handle and lock it into the 100cc position. **NOTE: DO NOT REPLACE THE COLORIMETRIC TUBE PRIOR TO THE SECOND 100cc PURGE CYCLE – YOU MUST USE THE**

SAME TUBE USED DURING THE FIRST 100cc PURGE OF THE ORIGINAL SAMPLE.

Read the calibration scale value aligned with the stained/unstained interface in the tube and use the pump stroke correction factors provided on the colorimetric tube instruction sheets to determine the correct reading for a 200cc purge volume.

8.0 Reading the Tubes

The basic AQR Color-Tec[®] method procedures are simple and intuitive; however, contaminant detection and semi-quantitative values are obtained through visual observation of the colorimetric reaction in the tubes, which is inherently subjective (especially in samples containing very low [$<5 \mu\text{g/L}$] total CVOHs). These low-level samples induce only a slight color change (i.e. slight darkening or light purple hue) prior to the 0.5ppm line on the tube scale at the entrance of yellow reagent layer in the LL tube. Samples containing concentrations of total chlorinated compounds above $5 \mu\text{g/L}$ usually induce a more apparent reaction within the LL tube.



8.1 Very Low Concentrations

When a sample contains very low concentrations ($<10 \mu\text{g/L}$) of chlorinated compounds, the resulting color change is not immediate or distinct. At these low concentrations the color change does not usually begin until 100 CCs of air have purged through the sample. Furthermore, the color change induced at these low concentrations is very slight (below 0.5 on the tube scale) and appears as a slight darkening or light purple hue at the entrance of yellow reagent layer in the LL tube.

8.2 Low to Medium Concentrations

When the sample contains higher concentrations ($>10 \mu\text{g/L}$) of chlorinated compounds, the resulting color change is an obvious light to dark purple, which propagates through the yellow reagent layer toward the pump end of the colorimetric tube. The detected concentration level is obtained by matching the linear extent of the discolored reagent inside the tube to the calibration scale printed on the outside of the tube.

8.3 High Concentrations

When the sample contains high concentrations ($>100 \mu\text{g/L}$) of chlorinated compounds, the color change reaction occurs quickly and usually exceeds the upper detection level of the Gastec[®] 133LL tube. The higher the concentration of chlorinated compounds in the sample, the faster the color change reaction occurs and the further it propagates through colorimetric tube. Samples containing percent-range concentrations ($>1000 \mu\text{g/L}$) of chlorinated compounds, often discolor the entire yellow reagent layer in the LL tube before the pump handle has been fully extended. In these cases, the purging can be discontinued to allow for the current sample bottle to be re-tested using a higher

range detector tube. There is no need to continue purging the sample when the detection level of the tube is exceeded. Each subsequently higher range tube is used to purge each new duplicate sample in succession until the color change reaction does not exceed the calibration range of the tube being used.

8.4 Recording Tube Readings

It is recommended to record the observed concentration value (tube reading), the range of the colorimetric tube (LL, L, or M), and the final purge volume when logging AQR Color-Tec® results. For example, a reading of 2.5 observed on an LL tube using a 100 ml purge should be recorded as **2.5/LL/100**. Purge volume correction factors must be applied for AQR Color-Tec® values which were obtained using any purge volume other than 100cc. For example, a reading of 0.2 observed on an LL tube using a 200 ml purge should be recorded as **0.1/LL/200**. A reading of 60 observed on an M tube using a 50 ml purge should be recorded as **150/M/50**. Purge volume correction factors for the 133 Series tubes are presented on Table 1 (pump stroke correction factors are also presented on the colorimetric tube instruction sheet included with the tubes).

Table 2
Purge Volume Correction Factors for 133-Series Tubes

Colorimetric Tube	Purge Volume	Quantity of Pump Pulls	Correction Factor
133LL	50cc	½	Tube Reading x 3
133LL	100cc	1	Tube Reading x 1
133LL	200cc	2	Tube Reading ÷ 2
133L	50cc	½	Tube Reading x 3
133L	100cc	1	Tube Reading x 1
133L	200cc	2	Tube Reading ÷ 2
133M	50cc	½	Tube Reading x 2.5
133M	100cc	1	Tube Reading x 1
133M	200cc	2	Tube Reading ÷ 2.5

9.0 Estimating Sample Concentrations

Although the AQR Color-Tec® method does not provide a specific measurement that directly quantifies the concentration in a sample, the level of intensity of a positive colorimetric tube reaction does provide a general indication of the magnitude of the concentration present in a sample (i.e. low, medium, or high). The colorimetric tube responses “readings” may be used to estimate the concentration of CVOHs present in a water sample only by comparing AQR Color-Tec® results to the results of split samples analyzed by GC/MS. Given a sufficient quantity of split sample pairs and sufficient range of

Table 3 Estimated Analytical Results for AQR Color-Tec® Values Less Than 10 (y = 52.62x + 5.44)	
AQR Color-Tec® Value (x)	Estimated Analytical Value (y)(µg/L)
0.1	11
0.2	16
0.3	21
0.4	26
0.5	32
0.6	37
0.7	42
0.8	48
0.9	53

concentration values, this GC/MS-to-AQR Color-Tec[®] comparison data can be used to obtain estimated concentrations for other samples which were analyzed only using the AQR Color-Tec[®] method. This can be achieved using linear regression analysis of the split sample comparison data. Given the site-to-site variability of factors that may affect the colorimetric response (such as the ratio of the various chlorinated compounds present), site specific comparison data sets are preferable over data sets collected from several different sites. The following is an example of a comparison performed using a groundwater sample data set collected from a drycleaner site in South Carolina:

To estimate total chlorinated solvent concentrations from AQR Color-Tec[®] readings, a linear regression analysis was performed using the results from 97 split water samples collected from the site, which were analyzed using both AQR Color-Tec[®] analysis and laboratory-based GC/MS analysis. Because the AQR Color-Tec[®] method does not distinguish between species of chlorinated solvents, the analytical results for solvent (PCE, TCE, Cis-1,2 DCE, Trans-1,2 DCE, 1,1 –DCE, and vinyl chloride) were summed to provide a total analytical result for chlorinated solvents.

Due to the nature of the AQR Color-Tec[®] method, the range of corresponding analytical values associated with each finite AQR Color-Tec[®] reading above zero is broad. For this reason, the regression analysis was performed for three ranges of color tech values: 0.1 to 0.9, 1 – 10, and >10. However, there were insufficient paired values for sample pairs exhibiting AQR Color-Tec[®] readings above 10 to estimate an analytical value. Table 1 provides the equation developed from the linear regression analysis for the 0.1 to 0.9 data range and the associated AQR Color-Tec[®] and estimated analytical values. Table 2 provides the equation developed from the linear regression analysis for the 1 to 10 data range and the associated AQR Color-Tec[®] and estimated analytical values. The “y” value is the estimated analytical value (µg/L) and the ‘x’ value is the AQR Color-Tec[®] reading. It should be emphasized that the analytical result calculated from the regression analysis is an estimate only. This estimate represents the central tendency. Actual analytical values may differ substantially from this estimate.

Table 4 Estimated Analytical Results for AQR Color-Tec [®] Values Between 1 and 10 (y = 49.88x + 18.63)	
AQR Color-Tec [®] Value (x)	Estimated Analytical Value (y)(µg/L)
1	69
2	118
3	168
4	218
5	268
6	318
7	368
8	418
9	468
10	517

10.0 Method Performance

A key item to note from comparison analysis is that an AQR Color-Tec[®] value of zero almost certainly represents an analytical result below most regulatory limits for chlorinated compounds. Further statistical comparison of the AQR Color-Tec[®] zero values with the split sample GC/MS data was performed to determine

Table 5	
Parameter (Total Chlorinated Solvents as Detected by GS/MS for AQR Color-Tec [®] Values of Zero)	Value
Mean (µg/L)	0.362
Range (µg/L)	0 – 2.55
Standard Deviation (µg/L)	0.736
95% UCL of the mean (µg/L)	0.857
90 th Percentile Value (µg/L)	1.626
95 th Percentile Value (µg/L)	2.37
Percentile less than 2 µg/L	93.4

the confidence of the AQR Color-Tec[®] zero values (non-detects or no response of the tube). This data set included 42 AQR Color-Tec[®] zero values. The percentile value was 93.4 for detection of total chlorinated compounds at 2 µg/L (i.e., AQR Color-Tec[®] detected 93.4% of concentrations detected by GC/MS at or above the MCL of vinyl chloride). The percentile value was 100% for detection of total chlorinated compounds at 5 µg/L (i.e., AQR Color-Tec[®] detected 100% of concentrations detected by GC/MS at or above the MCL of PCE and TCE).

11.0 QA/QC Procedures

To insure that consistent results and the lowest possible detection levels are achieved for all samples analyzed using this method, standard sample preparation procedures tailored to specific project goals should be developed by the user and followed precisely and consistently throughout the sampling and analysis program.

This section of the manual is intended only to provide the user with a basic methodology for conducting quality assurance/quality control (QA/QC) procedures for the AQR Color-Tec[®] method. Users of the method are encouraged to develop project-specific QA/QC and sample handling procedures that insure the level of consistency and accuracy required for the user's sampling program. This section presents some basic method-specific, QA/QC procedures developed to insure overall **method performance**, provide **analytical confidence**, identify potential **false positives** such as contaminants in the ambient air (since ambient air is used as the purge gas), and identify potential **false negatives** such as the presence chemical inhibitors that may be present in the samples or in the ambient air.

11.1 Method Performance and Analytical Confidence

Using the method to analyze 10ug/L, 50ug/L, and 100ug/L sample spikes will provide a comparison of AQR Color-Tec[®] readings to known concentrations, which provides a basis for estimating approximate concentrations in the field samples based on the AQR Color-Tec[®] responses. Testing of the higher range tubes using spiked samples is unnecessary because the high range tubes are usually not used unless the sample being tested has already exceeded the upper range of the low range tube, thus revealing that the sample being tested contains a sufficient quantity of chlorinated compounds to evoke a positive reaction from the next higher range tube.

11.2 False Negatives

The presence of Toluene and Xylenes inhibits/diminishes the ability of the colorimetric tubes to detect CVOHs. At sites where the presence of these compounds is suspected to be present in the samples or in the ambient air (since ambient air is used as the purge gas), QA procedures may include periodic testing of groundwater or soil samples and ambient air for the presence of toluene and xylenes using a Gastec[®] Toluene tube (the Toluene tube also detects xylenes).

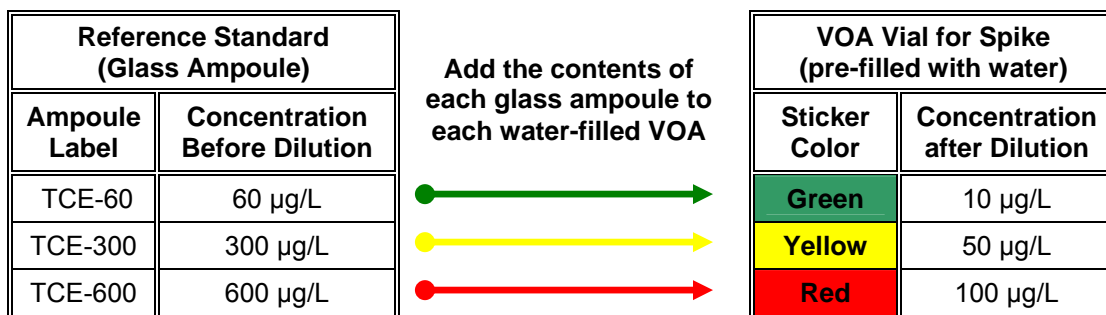
11.3 False Positives

Because the AQR Color-Tec[®] method uses ambient air as the purge gas, airborne chlorinated compounds at low concentrations can enter the sample and activate the detector tube. To prevent airborne contaminants from entering the sample and detector tube during sample purging and analysis, the method is used with a carbon pre-filter attached to the purge needle. To determine whether airborne chlorinated contaminants are present, a colorimetric tube may be used periodically to test the ambient air at the location where the field testing is being performed. If airborne contaminants are present

and the carbon filter is being used, the carbon filters can also be tested periodically using a colorimetric tube to determine if breakthrough is occurring. A build-up of water vapor in the colorimetric tube past the catalyst stage (black portion of the tube) can induce a subtle color change similar to that of a low-level positive result. This problem is easily avoided by observing the build-up of condensation inside the tube in the catalyst stage during purging, and stopping the airflow before the condensation reaches the end of the catalyst stage. This condition rarely occurs before the maximum required purge volume of 200 CCs is achieved and contaminant presence or absence has been determined.

11.4 Preparation of Spiked Samples for Method Performance QA/QC Tests

AQR Color-Tec[®] sample spikes are prepared by combining the Cerilliant[®] TCE reference standards (provided in the three 5 ml glass ampoules) with the pre-measured, analyte-free water (provided in the three VOA vials labeled with red yellow and green stickers on the caps). Transfer each reference standard (in the glass ampoules) to each water-filled VOA as follows:



After transferring the reference standards in the ampoules to the VOA vials pre-filled with analyte-free water, the VOA vials will contain TCE concentrations of 10 µg/L (green label), 50 µg/L (yellow label), and 100 µg/L (red label). These spiked samples are then analyzed using the AQR Color-Tec[®] method to analytical confidence. Spiked control samples are used to insure that the method is detecting the target compounds within reasonable limits and to provide a basis for estimating concentrations based on the AQR Color-Tec[®] responses.

Step 1 - Carefully break open the TCE-60 ampoule by inserting the ampoule into the plastic breaking collar and apply bending pressure against the neck of the ampoule using your thumbs and index fingers. The tip of the ampoule should break along the scored restriction in the neck of the ampoule.

Step 2 - After breaking the ampoule, use a clean 10 ml pipette to carefully transfer all of the liquid from the ampoule into the VOA vial containing analyte-free water marked with the green label. Tightly re-seal the VOA cap and shake the sample for 5 seconds to mix. The 10 µg/L spiked sample is now ready to pre-heat and test using the Color-Tec[®] method.

To prepare the 50 µg/L spiked sample, repeat steps 1 and 2 using the TCE-300 ampoule and the VOA vial containing analyte-free water marked with a yellow label.

To prepare the 100 µg/L spiked sample, repeat steps 1 and 2 using the TCE-600 ampoule and the VOA vial containing analyte-free water marked with a red label.

Important Note: Be sure to transfer all of the liquid in the ampoule to the VOA vial and use care to prevent any spillage of the liquid from the VOA vial. The liquid in the ampoules and VOA vials have been precisely pre-measured to result in 10 µg/L, 50 µg/L, and 100 µg/L sample spikes after mixing.

11.5 Method Performance QA/QC Test Procedure

Following preparation of the 10 µg/L, 50 µg/L, and 100 µg/L sample spikes, heat the spiked samples and three 133LL tubes as described in Section 4. After heating, conduct Color-Tec® analyses on the samples as described in Section 7 and record the results in your field log as described in Section 8. A positive result from testing the 10 µg/L spiked sample will confirm that the method is being conducted properly to detect low-level concentrations. The Color-Tec® readings obtained from testing the 10ug/L, 50ug/L, and 100ug/L sample spikes provides comparison to known concentrations to provide a basis for estimating approximate concentrations in the field samples based on the Color-Tec® responses.

11.6 Negative Interference (Xylenes/Toluene) QA/QC Test Procedure

To conduct a test for the presence of compounds which could inhibit the detection of CVOHs use the Toluene (122L) tube to analyze a duplicate soil or water sample using the procedures described in Sections 5 through 8.

11.7 Positive Interference (Ambient Air) QA/QC Test Procedure

To conduct a test for the presence of chlorinated VOHs in the ambient air, break the tips of a 133LL colorimetric tube and properly insert it into the hand pump. Pull and lock the pump handle into the 100cc position allowing ambient air to enter the colorimetric tube.

Note: Do not attach an extraction needle assembly to the colorimetric tube while performing this test. Once the 100cc flow cycle is completed, carefully read the tube and record the results. A positive result indicates the presence of CVOCs in the ambient air at concentrations detectable by AQR Color-Tec® which would affect sample results unless the carbon filter assembly is attached to the purge needle (see Section 6). A negative result indicates that CVOCs are not present in the ambient air at concentrations detectable by AQR Color-Tec® and therefore will not affect sample results. It is recommended that the carbon filter assembly is used regardless of the ambient air testing results.

11.8 Duplicate Sample Testing Procedure

Duplicate or replicate samples are collected from the same sampling location, at the same time, using the same collection methods, and analyzed using the same procedures as the original samples for the purpose of determining both sampling and analytical method variability. Since a second (duplicate) VOA vial is always collected for the Color-Tec® method, a duplicate or replicate analysis may be performed on the second (duplicate) VOA vial any time that a positive result (color change) is evoked by the original sample (first VOA vial) without exceeding the upper limit of the low-level colorimetric tube. In those cases, the duplicate or replicate analysis is simply performed by using a new low-level colorimetric tube to analyze the duplicate sample in the second (unused) VOA vial. If sampling and method variability is low, the result of the duplicate test will be the same or similar to the results obtained from the original test. The relative percent difference (RPD) may be calculated to quantify any variability in the results.

Note: The AQR Color-Tec® QA/QC Test Pack contains an extra low-level colorimetric tube to perform a duplicate or replicate analysis test.

12.0 Safety Precautions

As with the use of any product, it is recommended that the user carefully review all product manuals and Material Safety Data Sheets (MSDS) provided with this product prior to use. Several components of the AQR Color-Tec[®] kit are products obtained from other manufacturers which have manuals including safety precautions. Users of the AQR Color-Tec[®] method should carefully review the manuals and safety precautions and should become familiar with the proper use of all components included in the AQR Color-Tec[®] kit. It is recommended that the procedures involved with the method be incorporated into the user's Site-specific Safety and Health Plan (SSHP). MSDSs for all chemicals provided as part of the AQR Color-Tec[®] kit are available upon request or at <http://www.aqrcolortec.com>. The following precautions should be considered to reduce potential user safety risks associated with the performance of the AQR Color-Tec[®] method.

Activity	Potential Risk	Precaution
Breaking tube tips	eye injury, dermal puncture	safety glasses
Accidental tube breakage	dermal cuts, exposure to reagent	safety gloves
Use of purge/extraction needles	dermal puncture	use caution
Use of the hot plate	dermal burns, electric shock	limited setting
Use of PCE standards	dermal contact, dermal cuts	safety gloves

Additional Safety Notes:

- Use skin and eye protection while breaking colorimetric and carbon filter tubes;
- The thermostat dial setting of the Corning[®] Hot Plate should never be set above 5 for any heating purposes required by the AQR Color-Tec method[®];
- Do not over-fill the water bath pan while heating the samples and tubes;
- Always conduct sample and tube heating activities on a flat, stable, surface.
- Keep all flammable or combustible materials away from the Corning[®] Hot Plate during sample and tube heating activities.
- Always use the stainless-steel water-bath pan properly filled with water for heating the samples and tubes – do not heat samples or tubes directly on the surface of the Corning[®] Hot Plate;
- Do not use any heat source to heat the water-bath, tubes, or samples other than the Corning[®] Hot Plate provided in the hardware kit.

Disposal of Expendable Materials:

- Re-cap all needles before disposal;
- After re-capping each extraction needle, dispose of the extraction needle assembly while leaving the vinyl tubing attached to the colorimetric tube – Do not attempt to remove the extraction needle assembly from the tip of the colorimetric tube for disposal;
- Dispose of all sharps (needles and broken glassware) in accordance with any and all applicable local and/or federal rules or guidance.
- Dispose of all colorimetric tubes as specified in the Gastec[®] MSDS and/or in accordance with any and all applicable local and/or federal rules or guidance.
- Dispose of any remaining spiked-sample liquids as specified in the Cerilliant[®] MSDS and/or in accordance with any and all applicable local and/or federal rules or guidance.
- Dispose of all VOA vials used to contain sample materials in accordance with any and all applicable local and/or federal rules or guidance.

Table 6

Troubleshooting Guide

Problem	Possible Cause	Solution
Sample does not appear to be purging (bubbling) after the pump handle has been pulled.	Clogged/blocked purge (long) needle.	Use the decontamination syringe to check the purge needle for clogs. If clogged, clean the needle or use a new purge needle.
	Clogged/blocked extraction (short) needle.	Use decontamination syringe to check the extraction needle for clogs. Use decontamination syringe to clean the needle or use a new extraction needle.
	Colorimetric tube is not securely connected to hand pump.	Remove and re-insert the colorimetric tube from the hand pump. If the fit seems loose, replace the hand pump inlet gasket.
	Colorimetric tube is not securely connected to extraction needle tubing.	Check the connection between the extraction needle tubing and the colorimetric tube. If loose, insert the colorimetric tube further into the extraction needle tubing.
	VOA cap is not tightly sealed.	Check the tightness of the VOA cap. Tighten if necessary.
	Colorimetric tube tips were not broken before connecting to hand pump and tubing.	Break both tips of the colorimetric tube before connecting to hand pump and tubing.
	Broken/bad plunger seal in hand pump.	Check the pump seal by holding your finger over the hand pump inlet while pulling the pump handle and lock into the 50cc position. If no vacuum is apparent, open the pump, remove the plunger, replace the plunger seal, and grease the new seal. Re-assemble the pump.
The colorimetric tube shows no reaction after purging a sample that contains chlorinated compounds.	Colorimetric tube is below the optimum operating temperature.	Heat the colorimetric tube to 40°C/104° F before using. It is also recommended to heat the sample. The recommended temperature for tubes and samples when using the AQR Color-Tec [®] Method is 40°C/104° F.
	Colorimetric tube was connected using reversed flow direction.	Use the flow direction arrows to properly align the tube. The purged air must pass through the black oxidizer phase and the white catalyst phase before entering the yellow reagent phase.
	The sample also contains a detectable concentration of xylenes or toluene.	Samples can be tested for the presence of xylenes and toluene using the Gastec 122L colorimetric tube. The detection of chlorinated compounds may be diminished when xylenes or toluene are present in a sample.
The colorimetric tube indicates a reaction after purging a sample that contains no chlorinated compounds.	Chlorinated compounds are present at detectable concentrations the ambient air.	Test the ambient air using an LL tube to determine if chlorinated compounds are present at detectable concentrations. Attach the charcoal filter to the purge needle prior to purging samples.
	HCl vapor is present in the sample VOA or in the ambient air.	Avoid use of HCl in the area where AQR Color-Tec [®] is in use. Use only unpreserved VOAs for samples to be screened with AQR Color-Tec [®] .
	Water vapor has entered the yellow reagent phase of the tube indicating a positive reaction	NEVER purge more that 200 CCs through any sample. Stop purging before condensation inside the tube reaches the end of the black oxidizer phase. Avoid drawing any water from the sample VOA into the colorimetric tube.