An Innovative Field-Based Analytical Method For Low-Level Detection of Chlorinated Solvents in Groundwater and Soil Samples

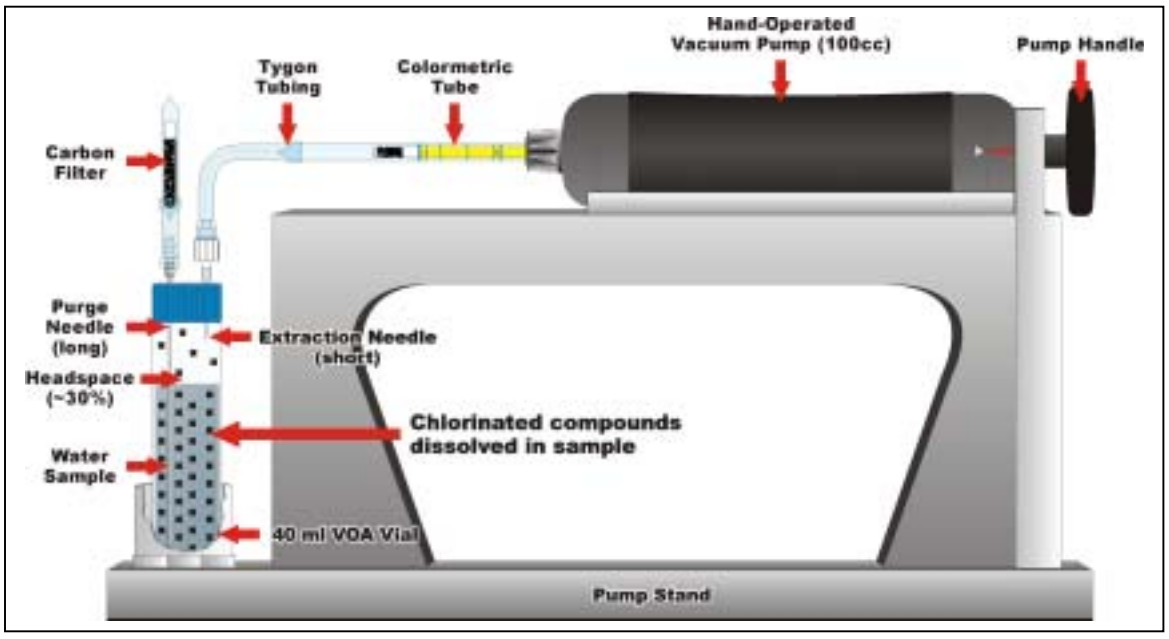
Abstract

Color-Tec is a field-based analytical method developed by Ecology and Environment, Inc. in 1997. The method combines the use of colorimetric gas detector tubes (originally designed for occupational breathing-zone monitoring) with sample purging to detect very low (*ppb-range*) concentrations of chlorinated compounds in groundwater and soil samples. The intended purpose of the Color-Tec method is to provide presence-or-absence (*i.e. qualitative*) information at or below regulatory levels for chlorinated compounds in groundwater and soil. Although, the method is semi-qualitative (*i.e. provides approximate concentrations*), the primary intent is to provide fast, low-level, low cost, decision-quality data that can maximize sampling frequency and sample coverage to identify and target "hot spots" at contaminated sites. This concept of utilizing real-time, low-cost, in-field measurement technologies to improve overall data quality is a key element of EPA's Triad approach to improved site characterization and cleanup by using multidisciplinary planning, flexible work plans, and on-site measurement technologies.

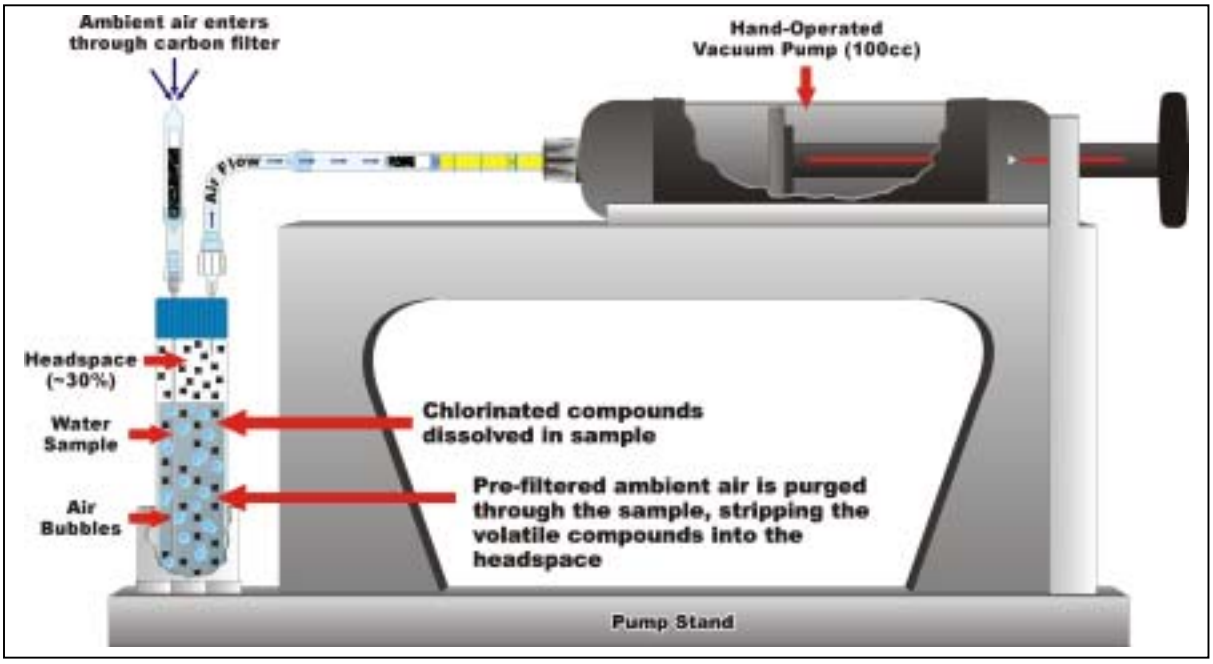
The Color-Tec method fits perfectly into this investigative strategy because it is intuitively simple, and the data are highly comparable to that of definitive laboratory-based analytical methods while being significantly less expensive per-sample than conventional laboratory analysis.

Method Description

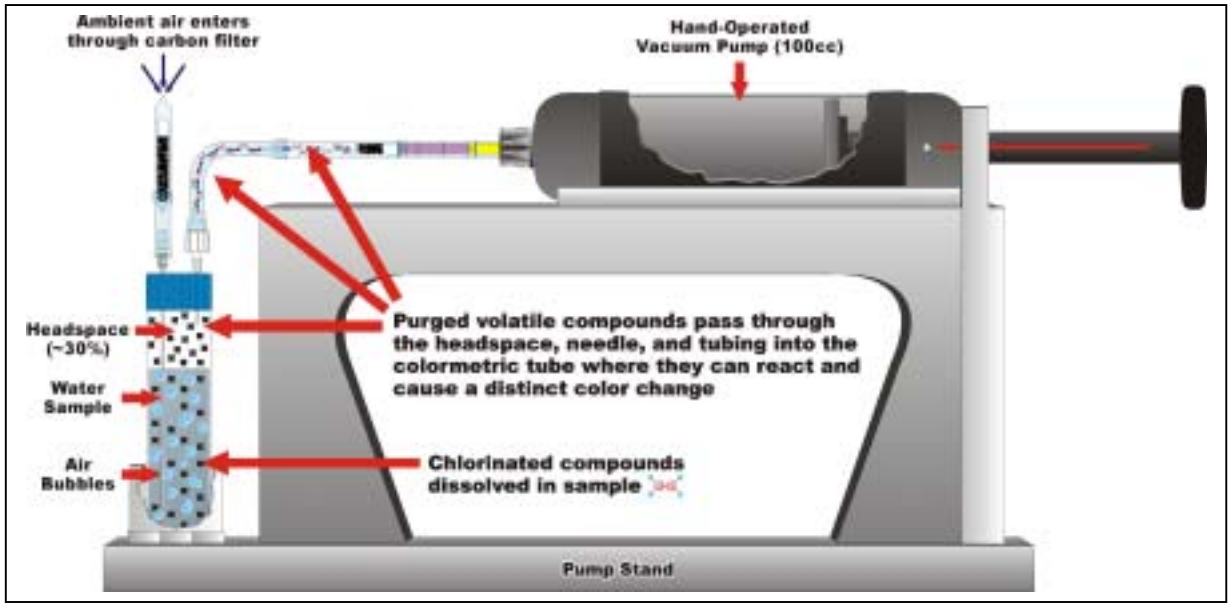
E & E's Color-Tec method combines a standard, commercially available colorimetric gas detector tube with a unique sample purging technique. This is achieved by using a hand-operated vacuum pump to purge the volatile compounds from a groundwater or soil sample through the colorimetric tube, which is designed to produce a distinct color change when exposed to chlorinated compounds. Each colorimetric tube contains an oxidizer that decomposes the chlorinated compounds entering the tube, releasing hydrogen chloride, which discolors the reagent in the tube. The tubes react positively to all chlorinated alkenes, and (to a slightly lesser degree) to the chlorinated 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.



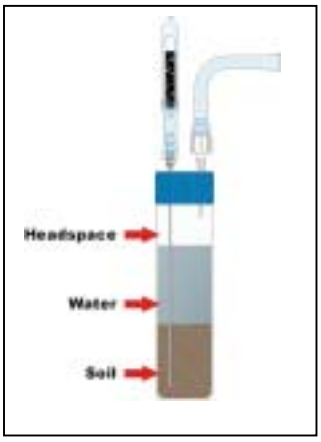
The colorimetric detector tubes are constructed of glass and printed with calibration scales to facilitate measurement of the linear extent of the color change reaction that occurs within the tube. To conduct the method, a standard 40-milliliter (ml) volatile organic analysis (VOA) vial is filled with the groundwater sample to approximately 70% capacity (leaving a 30% headspace) and tightly capped. The sample vial is then heated to approximately 40^{o} Celsius in a water bath.



Following heating, the headspace within the sample vial is connected to the colorimetric tube via a hollow, steel extraction needle attached to a short piece of Tygon® tubing. A second, hollow, steel, purge needle is inserted through the septa to the bottom of the VOA vial to facilitate purging. Using a manual vacuum pump, approximately 100 to 150 cubic centimeters of ambient air is purged through the water sample within the VOA vial directly into the colorimetric gas detector tube (*no water is to enter the colorimetric tube – only purge-air and contaminant vapors*). The purging process requires about 60 to 90 seconds to strip most of the volatile compounds from the sample.

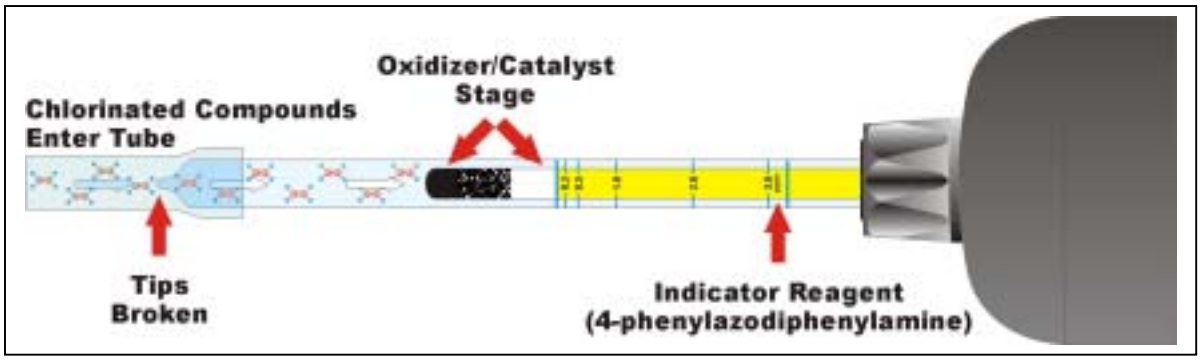


To analyze soil, sediment, or sludge samples using the Color-Tec method, approximately 25 to 35 grams of soil is placed into a VOA vial, followed by deionized water filled to approximately 70% capacity (leaving a 30% headspace) and tightly capped. The sample vial is then heated to approximately 40^{o} Celsius in a warm water bath. The analysis procedure is the same as with water samples.



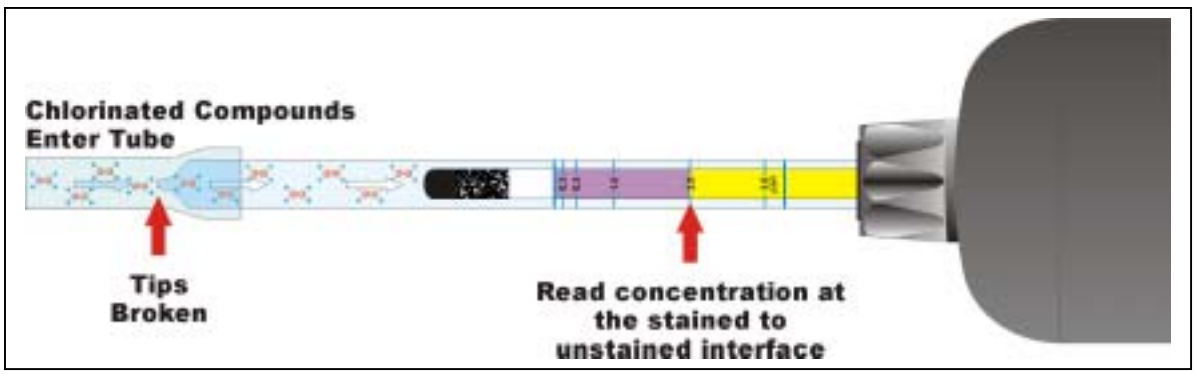
Colorimetric Tubes

The tube manufacturer (Gastec®) provides tubes for a variety of concentration ranges. The lowest concentration range tube is used initially to analyze the sample. When a positive result is observed, the 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. If the calibrated range of the tube is exceeded by the initial reaction, a tube with a higher concentration range is used to analyze a duplicate sample. This procedure is repeated until the approximate concentration is determined.



The colorimetric tubes and hand pumps used for E & E's Color-Tec method are manufactured by Gastec®, Inc. Each colorimetric tube contains a catalyst that decomposes chlorinated alkenes and alkanes, releasing hydrogen chloride, which discolors the reagent (4-phenylazodiphenylamine) in the tube. The reaction formula provided by Gastec®, Inc. for the PCE tube is as follows:

$$Cl_2C{:}CCl_2 + PbO_2 + H_2SO_4 \rightarrow HCl$$
$$HCl + Base \rightarrow Chloride$$



Gastec® provides tubes for identifying several specific chlorinated compounds including PCE, TCE, vinyl chloride, carbon tetrachloride, and methylene chloride. Because each of these tubes uses the same basic detection principle shown above, they will each react positively to all of the other chlorinated compounds.

It should be noted that the chlorinated compounds containing fewer chlorine molecules (such as vinyl chloride) induce a weaker reaction in the tubes than those compounds containing more chlorine molecules (such as PCE). Therefore, when a sample contains only vinyl chloride, additional sample volume and purge volume may be required to achieve the same color reaction as when the sample contains PCE. ***It is very important to note that because the colorimetric tubes react to all chlorinated compounds; specific chlorinated species cannot be distinguished using this method.*** Therefore, the values observed using the method reflect the sum of the concentration of each individual chlorinated compound present in the sample.

Tube Temperature. The detector tubes are designed to operate at temperatures between 0 to 40 degrees Celsius (°C; 32 to 104° Fahrenheit [F]) and are calibrated based on a tube temperature of 20°C (68°F). When the sample and/or the tube are above 20°C, the tube's sensitivity to the targeted compounds is increased. Conversely, when the sample and/or the tube are below 20°C, the tube's sensitivity to the targeted compounds is decreased. Therefore, to maximize the detection capability of the colorimetric tube, the samples and tubes should be heated to approximately 40 degrees Celsius before beginning the purging process.

Analytical Accuracy

The analytical accuracy of the Color-Tec method has been tested in two ways:

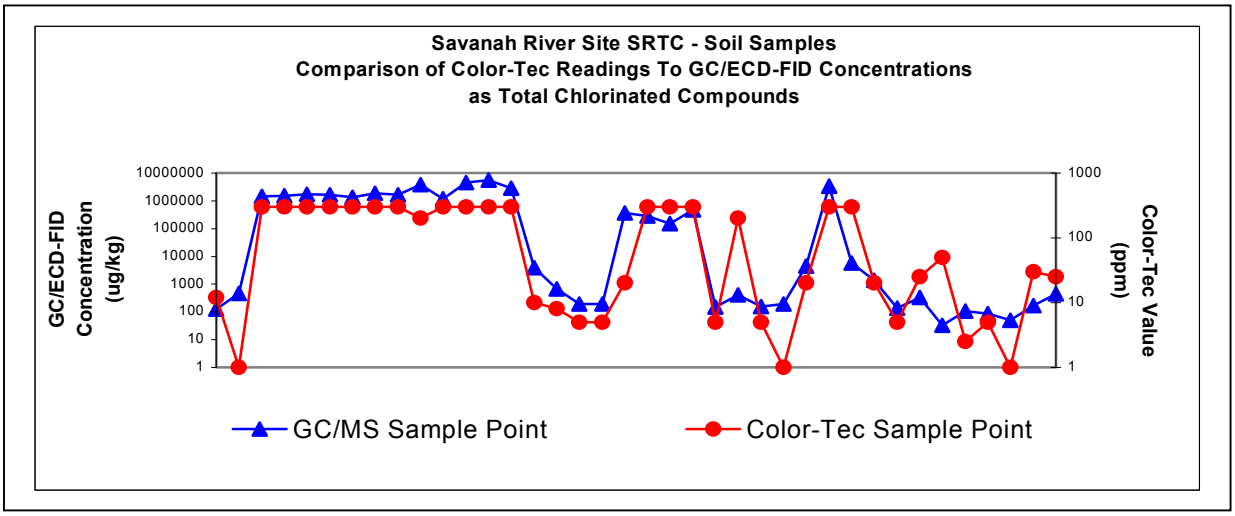
1. Comparison of colorimetric tube readings to pre-prepared, single compound, chemical standards (PCE and Vinyl Chloride only). This data set is relatively small, with less than 100 prepared samples tested with the Color-Tec method.

2. Comparison of the colorimetric tube readings of actual field samples to the GC/MS data from duplicates of those samples. This testing is on going as the method continues to be used. To date, approximately 2000 Color-Tec-to-GC/MS duplicate data pairs have been analyzed.

In the comparisons of the colorimetric tube readings to the pre-prepared standards, the method routinely detected PCE and vinyl chloride at concentrations of 1 µg/L and below. In the comparisons using the field-generated data, Color-Tec routinely detected total chlorinated compounds at or below the regulatory levels of the specific compounds detected by GC/MS analysis in the duplicate samples. The following table shows Color-Tec values detected in groundwater samples compared with the corresponding concentration ranges from duplicate GC/MS analysis of each sample. These data comparison sample pairs were collected from 8 drycleaner sites, which exhibited PCE, TCE, Cis-1, 2-DCE, and Vinyl Chloride in various ratios. The GC/MS values are expressed here as the sum total of the PCE, TCE, Cis-1, 2-DCE, and Vinyl Chloride concentrations detected in each sample. The total number of data pairs for each concentration range is shown in the column on the far right.

Detected Color-Tec Value (ppm)		Detected GC Concentration Range (µg/L)		Detected Color-Tec Value (ppm)		Detected GC Concentration Range (µg/L)	
Reading	Tube	Low	High	Reading	Tube	Low	High
0.1	LL	1	5	5	L	160	637
0.2	LL	2	34	10	L	239	2990
0.5	LL	2	71	15	L	101	3300
0.7	LL	9	111	25	M	290	43000
1	LL	8	234	100	M	2750	28000
2	LL	18	180	200	HA	8930	20000
3	LL	15	400	300	HA	14000	61920

The following graphs illustrate the relative comparison of Color-Tec readings (as recorded in parts per million [ppm]) from the scale printed on the tube) to the reported gas chromatograph concentrations (in µg/L) from the duplicate samples.

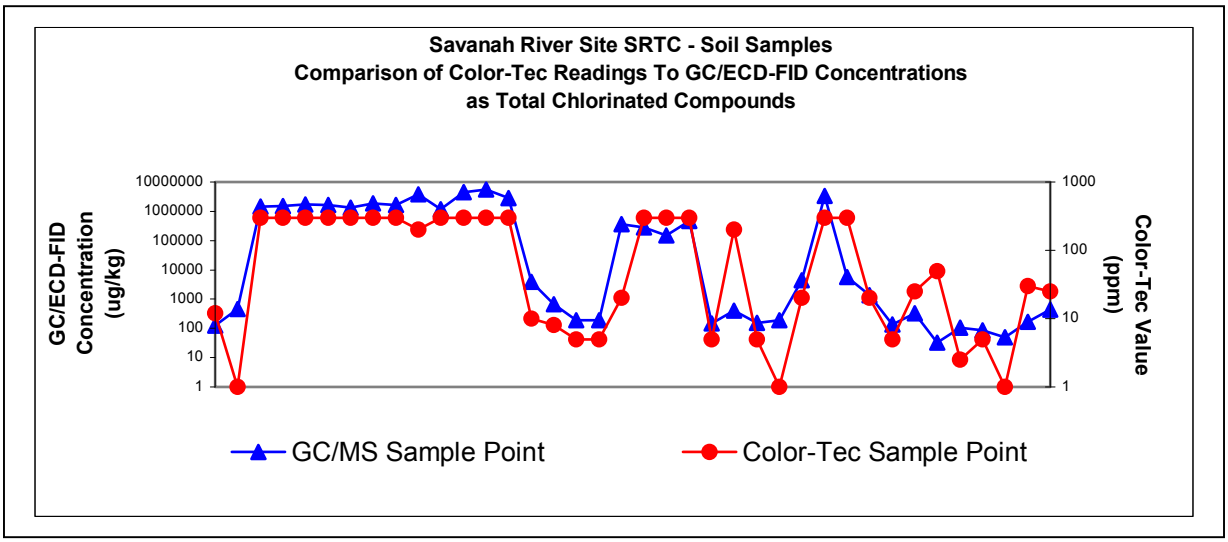


Potential Limitations

The Color-Tec method is intuitively simple to operate, requiring minimal practice to master. However, as with any analytical method, there are limitations, which must be considered by the user to effectively apply the method to the intended use while avoiding the collection of unrepresentative data.

- **Interference Compounds**

  Bromine, free chlorine, and hydrogen chloride also indicate a positive reaction in the colorimetric tubes. However, at most sites, these compounds are not likely to be present at sufficient levels to interfere with the detection of chlorinated compounds using the method. There is a remote possibility that a false-positive reaction could occur if the water sample being analyzed was preserved with HCL. Therefore, VOA bottles pre-preserved with HCl should be avoided.



The colorimetric tubes detect the sum total of all chlorinated compounds present in the sample. This interference from the other chlorinated compounds makes the identification of a specific chlorinated compound within the sample impossible. This is Color-Tec results are compared to the sum of all chlorinated compounds detected by GC/MS in the sample.

The presence of toluene or xylenes in a sample reduces the colorimetric tube's sensitivity to chlorinated compounds. For example, a concentration of 100 µg/L PCE in a sample that might normally produce a reading of 1.5 ppmv on the colorimetric tube, may only indicate a reading of 0.2 ppmv on the tube if a concentration of 100 µg/L toluene was also present in that sample. Therefore, the Color-Tec method is not recommended for use in areas where petroleum compounds are suspected or known to be present with the chlorinated compounds being targeted.

- **Observation of Color Change at Low Concentrations**

  The color change indicated by a sample containing less than 10 µg/L is very subtle. The solution to this problem is careful examination of each tube during and after purging.

- **Water Vapor**

  A build-up of water vapor in the tube past the catalyst stage 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 in the black catalyst stage of the tube during purging, and stopping the airflow when the condensation nears the end of the catalyst stage. The sample will most likely be thoroughly purged by the time this occurs.

- **Interrupted Air Flow**

  Thorough purging of the sample is critical for low-level detection. Therefore, the user must recognize and correct any problem that would decrease or interrupt the airflow through the sample and the detector tube, such as clogged needles and bad pump seals.

- **Airborne Contaminants**

  Because the method uses ambient air as the purge gas, airborne chlorinated compounds at low concentrations can enter the sample and activate the detector tube. The method may be used with a carbon pre-filter attached to the purge needle to prevent airborne contaminants from entering the sample and detector tube during sample purging and analysis. This modification is most useful during site investigations at or near active facilities (such as drycleaner sites and active industrial facilities) where the contaminant being tested for may possibly be released as vapor into the ambient air.

  We recommend that a carbon pre-filter be used for all Color-Tec method applications. The carbon pre-filter is a small, disposable glass tube packed with coconut shell charcoal (CSC). The carbon pre-filter is attached to the purge needle using a small section of tubing and a luer fitting. At most sites, a single pre-filter tube may be reused for several sample purges. However, at sites where high concentrations of airborne chlorinated compounds are suspected in the ambient air, the pre-filter tubes should be changed more frequently.

Color-Tec Analysis Applied to Other Compounds

Although the Color-Tec method is presented here in terms of detecting chlorinated compounds, the basic concept is theoretically applicable to other compound classes or (possibly) to other individual compounds. Gastec® and other colorimetric tube manufacturers (i.e. Dräger®) offer tubes designed for a wide variety of compounds. Although E&E has used the PCE tubes extensively for several years at numerous sites, our experience with applying the method to tubes designed for compounds other than chlorinated solvents is quite limited. When planning to apply the use of these other tubes with the Color-Tec method, special consideration must be given to the detection properties and potential chemical interferences of the tube being considered. Furthermore, testing using prepared chemical standards may be required to determine whether the selected tube will meet the analytical criteria of the project.

Using The Color-Tec Method

Complete Color-Tec kits, replacement parts, accessories, and Gastec® colorimetric tubes will be available by November 2003 from A.P. Buck, Inc. http://www.apbuck.com/

A.P. Buck, Inc.
7101 Presidents Drive
Orlando, Florida 32809
800-330-2825

For more information concerning Ecology & Environment, Inc.'s cost-effective, integration of field-based analytical tools into expedited site delineation and cleanup strategies contact:

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