

# STATE OF COLORADO

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*Dedicated to protecting and improving the health and environment of the people of Colorado*

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Colorado Department  
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## GROUNDWATER VOC SAMPLE PRESERVATION POLICY

The attached policy and statement of basis prescribe sample preservation methods for Volatile Organic Compound (VOC) analysis which will be used in compliance evaluation under Colorado Hazardous and Solid Waste laws, regulations, and permits.

Factors that led to development of this policy include: recognition that high concentrations of dissolved solids in groundwater is a widespread condition in Colorado; the knowledge that dissolved solids and other groundwater constituents often react with the acid used in sample preservation to yield inaccurate analytical data; and uncertainty within the regulated community over which method of sample preservation to use.

The attached policy specifies refrigeration as the approved preservation method for VOC groundwater samples. Several facilities in Colorado where these issues were identified earlier have adopted refrigeration-only preservation techniques for VOC groundwater samples which they have used for the past few years with great success. The policy specifies an exception for the collection of aromatic hydrocarbons (Benzene, Toluene, Ethyl Benzene, and Xylenes) which, due to their chemical characteristics, require collection of separate acidified samples.

Alternative preservation methods may be approved under this policy, in conjunction with 6 CCR 1007-3, Section 260.12(b), after the outlined steps are taken to demonstrate that the interaction between the sample preservation method and groundwater chemistry will yield accurate data.

The policy is accompanied by regulatory and technical rationale in the attached Statement of Basis.

<u>original signed by</u>	<u>original signed by</u>	<u>6/22/98</u>
Joan Sowinski Program Manger Federal Facilities	Gary Baughman Program Manager Compliance Program	Date

***(This document has been reformatted to improve accessibility in Portable Document Format (PDF). No other substantive changes were made unless specifically noted.)***

## **GROUNDWATER VOC SAMPLE PRESERVATION POLICY**

The following Technical Policy regarding the use of appropriate methods of groundwater sampling and preservation for Volatile Organic Compound (VOC) analysis, is established to provide necessary techniques to generate scientifically sound data that accurately represents aquifer groundwater quality. This policy will be used in the evaluation of facility compliance with Hazardous, and Solid Waste regulations, permits and statutes, involving groundwater sampling for VOC analysis. As explained in the attached statement of basis, the Division recognizes a substantial benefit from specifying a VOC sample collection and preservation standard, and as such has outlined the following policy as the Colorado Approved Method:

I. Groundwater samples shall be collected in bottles which do not contain any preservative, and shall be immediately inverted and placed into a pre-cooled device, and maintained at a temperature of 4° Celsius, plus or minus 2° Celsius through icing or refrigeration. Groundwater samples shall be maintained inverted, at a temperature of 4° Celsius, plus or minus 2° Celsius, from the time of collection of individual samples, until the time of analysis, for a maximum of fourteen (14) days. Upon retrieval from refrigerated storage, the laboratory shall document the presence of any gaseous void space, or “air bubbles”, and invalidate those samples with void space or “air bubbles”.

II. If groundwater samples are being collected to demonstrate aromatic hydrocarbons (Benzene, Toluene, Ethyl Benzene, and Xylenes), a separate sample shall be acidified to a pH less than 2 standard units with con Hydrochloric acid (1+1). The preservation pH shall be ascertained and documented by the laboratory using SW-846 method 9040 (pH, electrometric), or in the field by narrow range pH paper. Any and all physical effects such as effervescence, or sample heating shall be documented. Occurrence of any such physical effects will invalidate the sample (see Part III. below.) Barring occurrence of any such physical effects, the sample shall be immediately inverted and placed into a pre-cooled device maintained at a temperature of 4° Celsius, plus or minus 2° Celsius, through icing or refrigeration, and shall be maintained inverted, at a temperatures of 4° Celsius, plus or minus 2° Celsius, from the time of collection of individual samples until the time of analysis, for a maximum of fourteen (14) days. Upon retrieval from refrigerated storage, the laboratory shall document the presence of any gaseous void space, or “air bubbles”, and invalidate those samples with void space or “air bubbles”.

III. Where the criteria of Part II of this Policy cannot be met because of physical effects, the laboratory may analyze and report the concentrations of aromatic hydrocarbon VOCs using the unacidified sample.

IV. To maintain consistency and allow comparison of data, following publication of this policy, only the preservation method as described in this Policy, will be used throughout Colorado for VOC groundwater sample preservation. If an alternative sample preservation method is proposed, the regulation at 6 CCR 1007-3, Part 260.12(b) provides the information required to be submitted and the basis to be used for the Department review and decision.

## **BASIS FOR DRAFT POLICY MODIFICATIONS**

The following Technical Policy was released for public review September 27, 1996 in its draft form. Following the defined review period, all comments received were properly evaluated utilizing the professional judgment and experience of the Division. Those comments based upon appropriate scientific data, and believed to justify a change in the draft policy, were incorporated. As a result, the finalized Technical Policy differs in some respects from the original draft document. Following is a brief explanation of, and supporting basis for, each such change:

1: Section I of the policy provides for maintenance of collected ground water samples at a temperature of 4° Celsius, plus or minus 2° Celsius - a change from the issued draft which called for refrigeration at temperatures of less than or equal to 4° Celsius from time of collection. This modification was made in response to comments received which stressed the importance of allowing for field variability.

2: Section I of the policy provides for immediate inversion of the groundwater sample bottles, and maintenance of such inversion from time of collection until the time of analysis. This modification was necessary to address the concern regarding the possible formation of air bubbles in the sample bottles. Formation of such air bubbles can cause underestimation of dissolved gaseous Volatile Organic Compounds, and inversion of the sample bottles aids in facilitating their detection. In addition, the inversion of groundwater samples upon collection is a requirement of the audit program detailed in the OSWER Lab Inspection Guidance, by the Office of Solid Waste, and is routinely used by State inspectors as an audit inspection tool.

3: The issued draft included discussion of a method for demonstrating that an alternative sample preservation technique (i.e. acidification) may be acceptable. Such language has been excluded from the final Technical Policy as a result of the Hazardous Waste Commission adopting 6 CCR 1007-3, §260.12(b) in November of 1996 which provides a mechanism by which a party may demonstrate that an alternative sampling method other than refrigeration is acceptable at a particular site. Part C of the attached Statement of Basis discusses further such alternate sampling and analytical methodology.

4: Section II of the Technical Policy outlines the procedure to be followed if groundwater samples are also being collected to demonstrate the presence of aromatic hydrocarbons (Benzene, Toluene, Ethyl Benzene, and Xylenes (BTEX)). This section was added to the policy in response to comments received which supplied additional data clearly evidencing that sample degradation was more of a concern without acidification for these particular compounds. In addition, inclusion of this procedure for BTEX provides consistency with EPA methodology for these compounds, specifically EPA Methods 602 and 624.

## **GROUNDWATER VOC SAMPLE PRESERVATION POLICY STATEMENT OF BASIS**

Sampling of groundwater for the purpose of determining its quality and detecting the presence of hazardous waste constituents is a cornerstone of the Hazardous Materials and Waste Management Division (“the Division”) effort to identify releases, develop cleanup strategies, and measure the progress of remediation efforts. The objective of groundwater sampling is to obtain samples that accurately represent the quality of the groundwater in the aquifer and to determine the nature and the extent of contamination. To this end, the Division reviews and approves data acquisition plans, and conducts field, laboratory, and data inspections to determine compliance. These inspections are also designed to evaluate the utility, and appropriateness of data generated. The Division, and regulated facilities, have the obligation to systematically evaluate these plans, and to modify them in an effort to continually produce quality data. Regulated facilities must adhere to approved analytical plans. However, adherence to the plan with the knowledge that problems exist, may result in potentially negative consequences. As such, facilities also have an obligation to seek to modify such analytical plans when it becomes apparent that the plans will not function as designed. These modifications must be accompanied with appropriate rationale in order to justify and explain the necessity for such modification, and to the extent possible, lay a foundation for meeting project objectives. Any modifications to an approved plan must receive Division approval prior to implementation. Likewise, the Division carries the ongoing responsibility of conducting follow-up evaluations, on all previously approved documents, to ensure they maintain the appropriate level of utility, and continue to produce data of suitable, scientific quality. Such individual evaluation is necessary due to the vast amount of contaminant, groundwater type, lithology and contaminant combinations possible.

### **A. REGULATORY DISCUSSION**

A review of the Colorado Hazardous Waste Regulations, 6 CCR 1007-3 and the Federal RCRA Regulations, 40 CFR, for sampling requirements, reveals fourteen specific citations pertaining to requirements for a particular analytical method, or set of required methods. In general, these instances refer to specific RCRA methodology (“SW-846”) for which there are no equivalent substitutions such as the Paint Filter Test for determining free liquids in waste, the Toxicity Characteristic Leaching Procedure (“TCLP”) required for making hazardous waste determinations, and for compliance with the disposal standards for characteristic wastes, metal and cyanide bearing listed wastes. Otherwise, the regulations do not contain requirements for the use of specific analytical methodology. This absence of requirement is the basis for the flexibility essential to both permit writers and corrective action specialists, in writing facility specific permits and orders. Similarly, the Colorado Regulations Pertaining to Solid Waste Disposal Sites and Facilities, 6 CCR 1007-2, requires groundwater analytical methods to be in accordance with Division guidelines, or EPA approved methodology (Appendix B(3)B), and advise that SW-846 may not always be the most suitable for analytical monitoring (Appendices I & II).

Although the use of standard methodology may be less complicated, there are facilities in Colorado which operate a variety of analytical methodology, including RCRA, Contract Laboratory Program (“CLP”), Clean Water Act, Safe Drinking Water Act, and ASTM methods,

to name a few. Adopting one set of methods to create uniformity fails to recognize the influences of contaminant and environmental combinations, the advantages, and the availability of each individual analytical method. It is the existence of such situations that compels the generation of this policy to aid the Division in tailoring analytical plans to meet project specific goals while addressing site specific characteristics.

The Division believes that this policy is consistent with overall EPA RCRA implementation goals for Colorado and the nation. In November 1996, the EPA Office of Solid Waste, under a mandate from the executive branch to reinvent government, stated its objective to foster innovative approaches and pertinent application of SW-846 by defining its position that SW-846 was a guidance document except where program defined applications were necessary (e.g., Paint Filter Test, TCLP). This position was further articulated in October of 1997 when the EPA announced its intention to require a Performance Based Measurement System applicable to all programs, and specifying that all programs must define a performance based approach to environmental measurements. (FR 62, No. 193, p 52098, Oct 1997)

## **B. TECHNICAL DISCUSSION**

The Division oversees the installation of groundwater monitoring wells either to investigate contaminant migration, or to demonstrate that contaminants have not entered the groundwater; unlike drinking water wells installed for more palatable attributes, these monitoring wells are installed in locations that would be considered unacceptable for such consumption, such as, down gradient from a land disposal unit. These groundwater monitoring wells are installed to depths that intercept strata that do contain, or may contain water, and, therefore, constitute potential migration pathways. Consequently, these waters may become influenced by these strata, or solid wastes.

In many areas where monitoring wells are installed, the groundwater does not meet federal water quality potability guidelines due to a high solids content. Groundwater samples taken from monitoring wells are typically grab samples and, as such, the samples often include a solid phase and dissolved solids. These solids may include carbonate salts; oxides and hydroxides of alkaline, alkaline earth or transition metals; and clays and silicates, all of which can act to neutralize artificial acidity, or act as a buffer to added acidity. It has been observed and reported in Colorado, that some of these samples react immediately with an acid preservative and produce an effervescence. Failure to achieve the desired preservation pH, of less than 2 standard units, has also been observed and reported in Colorado. High concentrations of sulfate are often found in groundwater samples which, with the presence of Iron or Zinc and with the addition of acid, can produce a reducing environment. The potential to create a rigorous reducing environment may also cause reductions of unsaturated halogenated VOCs such as Vinyl Chloride, TCE, and DCE to less toxic halogenated VOCs which would create artifacts in subsequent risk assessments. It has been reported in Colorado that certain groundwater produces sulfurous odors when acidified. These reactions are uncontrollable and, to a certain extent, unpredictable. This leads to concern about the uncertainties associated with these physical and chemical properties, and their effect on the scientific validity of the data generated. To avoid unacceptable losses of those halogenated VOCs (e.g., Vinyl Chloride) which are dissolved gases in the groundwater sample into a void space, samples must be collected without headspace, or "air bubbles".

Obtaining such samples is difficult, often requiring repeated attempts at filling the sample vial. Consequently, acid previously added would be lost or diluted, and the samples collected would vary in pH. Sample heating from interactions with added mineral acid preservative has been observed and reported in Colorado, and is a particular concern because of potential losses of dissolved, gaseous VOCs which are typically the most toxic and mobile target compounds. These gaseous VOCs are collected from aquifers which are at an average temperature of 14° Celsius, and typically cooled to 4° Celsius until ready to be analyzed. Then the bottles are allowed to warm to room temperature (approximately 23° Celsius) prior to subsampling, or obtaining an aliquot. The propensity of these gaseous VOCs to move into a void space is at a minimum when the samples are cool, but significantly higher when the samples are opened for analysis. These complications which cause variations in sampling precision, and decrease the scientific quality of the data generated, have been observed in Colorado and lead to a concern that volatile concentrations may be underestimated, and are therefore not representative of ground water quality. It has also been observed and reported in Colorado that acidified duplicate sample pairs have a wider sampling precision interval than unpreserved duplicate sample pairs as calculated by the Relative Percent Differences between the sample duplicate pairs.

The Division has a further concern about the rigor applied to make analytical methods conform with the scientific method when acidified samples are measured against blanks, controls, and calibrants which are not also acidified, and the fact that matrix and surrogate spikes are introduced into a sample matrix just prior to analysis. The Division believes that the scientific method is best applied when all of the variables are held constant, except the variable (volatile concentration) being measured. The potential for introducing systematic error, or discriminatory conditions, without detection, does exist. It has been observed and reported in Colorado that the use of acid preservation in groundwater monitoring samples discriminates against certain compounds and/or classes, such as: certain chlorofluorocarbons, or Freons used principally in industrial and domestic refrigeration units which make their way to solid waste units; oxygenated hydrocarbons (ketones, alcohols, and ethers); and certain halogenated hydrocarbons (1,2-Dichloropropane, Vinyl Chloride). When these compounds are present at low concentrations, there appears to be a higher probability for detection when the samples are not acidified.

The cause of errors, or unrepresentative results, may be due to physical or chemical influences introduced at sampling, or at analysis. Acid catalyzed or enabled chemistries are possible for some of the VOCs, which may involve decomposition (Freons and 1,2-Dichloropropane), or transformation (Vinyl Chloride). The mechanisms that cause underestimation of VOCs in groundwater samples are complicated due to the complex nature of the groundwater; the contaminant and combination of contaminants; the dissolved solutes and the undissolved solids; and the interactions between each of these components and added mineral acids. Furthermore, anaerobic biological degradation of halogenated VOCs may occur over several decades for an aquifer, not in several days in a sample taken from an aquifer. Aerobic biological degradation of halogenated VOCs is not a credible concern for samples taken from an anaerobic aquifer, immediately hermetically sealed and refrigerated, and stored until analysis without gaseous void space, or “air bubbles”.

Solid waste managed in a land unit decays by microbial and atmospheric processes which are typically oxidative. Oxidation of organic solid waste produces Carbon Dioxide which, in water, rapidly transforms into Bicarbonate. Solid waste units impacting groundwater show elevated concentrations of dissolved Carbon Dioxide and Bicarbonate at monitoring well locations. It has further been reported and observed in Colorado that impacts of volatiles to groundwater from these sites elevate during episodic rises in Bicarbonate groundwater concentrations. The influence of a regulated land unit on the native character of groundwater thus includes imparting chemical and physical attributes. These inorganic carbon species derived from degradation of solid waste acting alone, or in concert with geological sources, can strongly influence acid-base chemistries described previously, and become a concern.

Three land disposal units in Colorado, with historical acidified sample data showing no groundwater impact from VOCs, subsequently exhibited evidence of VOCs above the Groundwater Protection Standard when the operators were directed to collect VOC samples without acidification on the next sampling event. The Division finds compelling evidence from these three examples that acidification of VOC samples adversely impacts analytical results.

### **C. DESIGNATED ALTERNATIVE METHODOLOGY**

The Division is committed to acquiring data that is scientifically sound and facilitates an understanding of the quality of the environmental medium, and the chemical and physical properties of any hazardous waste present, in the environmental sample of interest. Therefore, the Division will allow, or may require alternative sampling and analytical methodology.

The Division has, in the past, allowed for the use of alternative sampling and analytical methods when: (1) a high probability of danger exists in analyzing samples, (2) the existing methodology did not address the parameter of interest, (3) the alternate method excelled in performance and minimized interferences, (4) the alternate method met the data quality objectives of the project at a lower cost, or (5) the alternate method was available. This policy reiterates a Division commitment to entertain innovative equivalent approaches where available. This commitment is found in the Colorado Hazardous Waste Regulations, 6 CCR 1007-3, Section 260.12 which specifies that alternate analytical methodology is allowed, and provides the process for implementing such alternative methods. The Division has required, and will continue to require, alternate sampling and analytical methodology in cases where existing methodology does not, or cannot meet the data quality objectives of a given project, or fails to perform in a given circumstance.

This policy recognizes that the adoption and implementation of a Performance Based Measurement System can be challenging; in that, the Division has the commitment to consider applicability, safety, availability, and cost in the selection of sampling and analysis, but also serves a mission to preserve and protect the environment. Given the desire and commitment to allow the maximum flexibility in the selection of sampling and analytical methodology, the Division must look at those areas where rigor and standardization would be beneficial. Because of this, the Division recognizes substantial benefits from specifying a VOC sample collection standard for groundwater sampling. These benefits are discussed in the Regulatory and Technical Discussion sections of this Statement of Basis.

The Division has therefore formulated the following sampling standard: the collection of groundwater in sample bottles which do not contain preservative, from monitoring locations installed in and around permitted, interim status, or corrective action land units, subject to the Solid Waste Regulations, or the Hazardous Waste Regulations, with a specification for refrigeration of a VOC sample immediately upon collection to a temperature of 4° Celsius +/- 2° Celsius. This standard requires preservation by refrigeration for a maximum of 14 days, at 4° Celsius +/- 2° Celsius, or until analysis, whichever comes first, a method that has been proven reliable in obtaining accurate and precise sampling results.

It has also been observed and reported in Colorado, and elsewhere in the nation, that aromatic hydrocarbons (Benzene, Toluene, Ethyl Benzene, and Xylenes) can show significant biological degradation and subsequent underestimation when samples are not preserved. When aromatic hydrocarbons are contaminants of concern, a separate sample shall be collected, and acidified to a pH of less than 2 standard units with conc Hydrochloric Acid (1+1) for analysis of such aromatic hydrocarbons. The preservation pH shall be ascertained by SW-846 method 9040 (pH, electrometric), or by narrow range pH paper. Any, and all physical effects such as effervescence, or sample heating in a groundwater sample shall be documented as observed in the field, and shall cause the sample to be invalidated. The presence of gaseous void space, or "air bubbles" in any groundwater sample shall also cause the sample to be invalidated.