



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
SOLID WASTE AND EMERGENCY
RESPONSE

MEMORANDUM

SUBJECT: Appropriate Selection and Performance of Analytical Methods for Waste Matrices Considered to be "Difficult-to-Analyze"

FROM: Barnes Johnson, Director *Barnes Johnson*
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TO: James Berlow, Director
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The Waste Treatment Branch of the Hazardous Waste Minimization and Management Division has asked for our advice concerning several comments from industry regarding waste matrices that they consider to be "difficult-to-analyze" when certain RCRA analytical methods are used.

Although in seemingly different circumstances, the same inference has been specifically made in the following specific analytical situations (other situations may also be pertinent):

- 1) analysis for total organic constituents in treatment residues from certain kinds of stabilization processes that have utilized activated-carbon as an adsorptive reagent;
- 2) TCLP analysis for lead in foundry sands that have had iron filings added; and
- 3) analysis for total cyanide in cyanide-bearing plating wastes that have been treated with polysulfides.

The label of "difficult-to-analyze" has been placed on these waste matrices due to industry's interpretation of the results of their quality assurance performance data. Apparently, some of these data indicated very low percent recovery of some analytes from waste samples spiked with the constituents of interest (based on the analytical conditions used).

In all of the aforementioned matrices, chemicals or materials have been intentionally added for the purpose of "treatment" (carbon, iron, and polysulfides, respectively). These reagent-like additives have been either specifically identified in the published analytical methods as causing interference with the analysis or would logically be expected to cause interference by their known physical-chemical properties. In fact, it is these physical-chemical properties that are the basis of the claims of "treatment". As a result, one would actually expect to see analytical performance problems such as low recovery of spiked target analytes arising during routine application of certain methods. These then need to be "corrected" either by using an alternative method (i.e., one with the same objective of analysis such as the measurement of "total" constituent concentrations) or by modifying the analytical conditions of the method being used.¹

The concept of "difficult-to-analyze" matrices can then be translated into either "improper selection of analytical methods or conditions" or "not able to analyze with existing validated methods". In the latter case, there may actually be either no published analytical methods that may be considered "appropriate" or none that have been fully validated. In such cases one has the choice to either develop and perform a methods development/validation study² or evaluate alternative mechanisms (such as a research study to investigate alternative process controls or acceptable surrogate analyses) to validate the objective of the data gathering.

This is true whether the objective for the RCRA data gathering effort is, for example, to 1) demonstrate compliance with a published RCRA treatment standard; 2) demonstrate that a waste is either RCRA hazardous or nonhazardous; 3) assess the extent of chemical contamination in an environmental matrix for a RCRA clean-up; or 4) perform a research and development treatability analysis for RCRA.

If the specific objective of the RCRA data gathering is to prove that "treatment" is occurring, low recovery of target

¹Analytical parameters in SW846 methods are generally considered as guidance and may be adjusted to enhance method performance. These parameters include longer extraction times, smaller (or larger) sample sizes, choice of extraction reagents, and addition of chemicals to counter the known interferences. Parameters that may not be adjusted without adversely affecting method performance are identified in the methods.

²OSW has developed guidance for using a generic method validation procedure for cases where an appropriate analytical method has been developed but has not been formally validated for extensive use.

analytes may very well be a strong indication that some form of "treatment" has occurred. It is scientifically logical to expect that if the physical-chemical properties of the additives are such that the constituents of interest would be either destroyed or adsorbed by the reagent-like additives and there is an excess of those additive present in the waste matrix being analyzed, then one cannot expect the quality control data to show acceptable recovery of target analytes spiked into this matrix. These reagent-like additives can also interfere through physical and chemical interactions with the extraction reagents or other analytical agents that are critical to successful analysis.

The fundamental problem in these circumstance is, however, that the absence of adequate recovery data essentially invalidates the analytical data that are obtained. Owing to these unacceptable recovery data, *there is no assurance that any positive concentrations measured in these samples reflect real values.* This is particularly true if a positive value is measured when excess reagent-like additives are known to be present. As such, demonstration of compliance with a RCRA regulatory limit (such as a concentration-based treatment standard under the Land Disposal Restrictions³) may be precluded for that truly "difficult-to-analyze" matrix.

This memorandum also clarifies what *has been* the Office of Solid Waste's (OSW) position on what it considers to be appropriate performance for analytical methods when used for the RCRA Program. The concepts underlying these statements have appeared in various forms in our peer-reviewed analytical methods publications. Specific references to adequate recovery data for some selected RCRA methods and matrices are included in SW846. Additional references on adequate recovery data can be found within the specific published analytical method. OSW's position continues to be that:

Inadequate recovery of target analytes from the RCRA-regulated waste matrices of concern demonstrates that the analytical conditions selected are inappropriate for the intended application. Proper selection of an appropriate analytical method and analytical conditions (as allowed by the scope of that method) are demonstrated by adequate recovery of spiked analytes (or surrogate analytes) and reproducible results. Quality control data obtained

³This is also consistent with the justification underlying EPA's establishment of technology-based treatment standards as alternatives to concentration-based standards. This also forms the basis of the granting of treatability variances based on compliance with specified process controls or other surrogate constituents or waste characteristics. In cases where measurements are required demonstration of adequate quality assurance/quality control is necessary for demonstration of compliance.

must also reflect consistency with the data quality objectives and intent of the analysis.

1. Proper Selection of an Appropriate Analytical Method:

It is also important to point out that in most RCRA applications, OSW does not actually require the use of analytical methods published in *Test Methods for Evaluating Solid Waste*, SW-846. For these applications, the analyst may use "any reliable method" which can meet the project-specific data quality objectives designated for a specific application, as delineated in the Quality Assurance Project Plan for that particular application. For the few applications under 40 CFR Parts 260-270 where SW-846 methods must be used, it is OSW's intent, except for the cases where the method defines the regulation, e.g., hazardous waste characteristics, that the methods may be modified, as needed, to achieve the data quality objectives required by the specific RCRA application, e.g., permit compliance. This allowance for flexibility is explicitly stated in the Preface and Overview of SW-846:

"The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes."

2. Acceptable Recovery of Spiked Target Analytes

The analyst must demonstrate that the analytical method chosen, whether or not it is published in SW-846, generates adequate recovery data for the target analytes for the data to be acceptable for RCRA purposes. OSW guidance on method modification to achieve adequate recovery is included in the Disclaimer and Chapter Two of SW-846 and in the OSW document, "Guidance for Methods Development and Methods Validation for the RCRA Program". For methods development (i.e., validation) activities, recoveries from relatively clean matrices should be in the 80-120% range.

- a) For extractable organics in standard RCRA matrices, e.g., groundwater, aqueous leachates, soils, OSW considers a sample preparation method appropriate for use if it generates an analyte recovery of 70% or greater (Method 8270C, Sec. 1.1).

For extractable organics in "difficult matrices", e.g., sludges, ash, stabilized wastes, OSW considers a sample preparation method appropriate for use if it generates an analyte recovery of 50% or greater.

- b) For volatile organics, using relative recoveries, i.e., standard curves established by purge-and-trap, headspace, or other preparation of standards, OSW considers a sample preparation method appropriate if it generates a relative analyte recovery of 80% or greater (Method 8260B, 8015B).
- c) For inorganic analytes in almost all matrices, an absolute recovery and precision of 80-120% can generally be achieved with the proper choice of acid digestion procedure and determinative method for the analyte of interest.

If you have any specific questions on the performance of a given method for a particular waste matrix, please contact our Methods Team at 202-260-4761. For specific questions on analysis for organics contact Barry Lesnik, RCRA Organic Methods Program Manager, and for questions on analysis for inorganics contact Ollie Fordham, RCRA Inorganic Methods Program Manager.