FIELD INVESTIGATIONS OF UNCONTROLLED HAZARDOUS WASTE SITES

FIT PROJECT

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DRAFT

INTERIM REPORT
ON A
PROTOCOL FOR FIELD CHARACTERIZATION
OF HAZARDOUS WASTE

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SECTION 1: INTRODUCTION

This report provides consecutive methods for field characterization of hazardous waste. It is predicated on the assumption that initially nothing is known about the waste at a site. Obviously, this will not always be the case. There will sometimes be much available information on the history of a site and the wastes which have been disposed there. It is very important to exhaust all background information resources and complete off-site reconnaissance before an attempt is made to enter a site and begin waste characterization.

The scheme discussed in this report is designed to allow waste samples to be safely collected and rapidly characterized for safe compositing and further laboratory analysis. In addition, it will provide laboratory personnel with valuable information and a head-start on the analysis of the waste. It is devised to merge with a laboratory analysis scheme such as the one being developed by the Region VII EPA laboratory. Together the procedures will help fill in the gaps existing in the EPA priority pollutant analysis procedures which were not designed with the intent to completely analyze a hazardous waste as is desired for safe cleanup of waste sites and is required by the Resource Conservation and Recovery Act (RCRA).

SECTION 2: SAFETY

There are numerous safety considerations which must be addressed when preparing to obtain a sample and conducting an analysis procedure. The tests outlined in this procedure have been designed to allow for the separation of incompatable wastes and provide information necessary for safe laboratory analysis as well as waste staging and removal operations. The greatest danger to field personnel exists from the time an attempt is made to open a closed container or obtain a sample until the waste has been characterized to sufficiently assess the particular hazards of the waste. Drum opening procedures and necessary safety measures are currently being developed. All tests in the field portion of the analysis are to be conducted a safe distance upwind from the site and only with a small sample of the waste. All contaminated sampling and characterization materials and protective gear must be decontaminated or disposed of properly. Some additional safety considerations unique to specific tests will be addressed later in the discussion of the procedure.

SECTION 3: DOCUMENTATION

It is very important to develop a documentation procedure to be initiated at the beginning of the waste characterization and continued throughout the analysis procedure. There are many methods of documentation which can be used as long as it identifies each waste or container and allows each sample to be traced throughout its analysis.

SECTION 4: PROCEDURE

The characterization and analysis procedure is divided into several sections, beginning with a site characterization section for safety. Each section consists of several steps or tests. The analysis procedes consecutively through the steps unless as a result of a test the procedure directs the analysis to another section or step, or the sample is included into one of the waste categories listed below.

Typical Waste Categories

Group I:	Air Reactive	Group VII:	Cyanide & Sulfide Wastes
Group II:	Solids	Group VIII:	Inorganic Bases & Neutrals
Group III:	Water Reactive	Group IX:	Organic Oxidizer
Group IV:	Inorganic Oxidizer	Group X:	Organic Acids
Group V:	Nitric Acids	Group XI:	Organic Bases & Neutrals
Group VI:	Inorganic Acids		

The above categories are not all inclusive, therefore, at some major sites similar to Chemical Control, Elizabeth, N.J., or Seymour Recycling Center, Seymour, Ind., additional groups may be added such as radioactive wastes, gas cylinders, resins and prepolymers, etc. On the other hand, at smaller sites often only a few of the categories will be represented and sometimes only one waste will be present. It is not possible to design a characterization procedure which is suited to every site. Sometimes portions of the procedure may be omitted or additional tests may need to be added. Care must be taken when deleting steps not to omit a step which is necessary to determine the safety of a step which it procedes. Each site needs to be considered individually.

A narrative of the general categories and the analysis steps which they include begins below. A condensed outline of the procedure which numerically lists the analysis steps begins on page 14.

A. Site Entry and Safety Characterization

Site entry procedures will vary on a case by case basis depending on the nature of the site and how much is known about the site initially. If there is ever any question over what safety measures or personal protection is necessary, the higher level of protection should always be used until sufficient information is obtained to deem the precautions unnecessary.

Several indispensable monitoring and survey instruments are an explosive atmosphere meter, oxygen meter, draeger pump with hydrogen cyanide tubes, radiation survey meter, and an organic vapor analyzer (OVA) or HNU photoionization detector. There may be additional survey equipment necessary at particular sites other than those listed above, such as a metal detector or additional gas detector tubes. The radiation survey meter should be equipped with a probe which is sensitive to alpha particles in addition to beta and gamma radiation. At many sites each container will have to be scanned for radioactivity after it is opened. All radioactive wastes should be segregated for safety purposes and properly labelled to meet shipping requirements. The HNU photoionization detector is not sensitive to several flammable organic vapors such as methane, ethane and propane, therefore, its use as a safety monitoring instrument is limited. A Century organic vapor analyzer may be used for explosive atmosphere monitoring unless the vapor concentrations are higher than the instruments full scale, at which time a less sensitive explosion meter must be employed.

B. General Visual Checks and Physical Characteristics

The steps in this characterization phase are very broad and will differ greatly from site to site. All pertinent meteorological information and geological characteristics should be recorded. A complete inventory of the site may be conducted including the types and quantity of containers present. Any customized containers or suspicious looking drums should be noted for special handling and segregation. Record any evidence which indicates the toxicity of the waste or potential hazards such as dead plants or animals or bulging drums.

C. Sample Acquisition

Great care is required when opening drums or any sealed container. A detailed drum opening procedure is not within the scope of this paper, however, several methods are currently under development.

The air reactive wastes will be discovered during the opening or sampling procedure. The air reactive substances normally require special packaging. The wastes may be stored under water or some other liquid to prohibit air from coming in contact with the waste. They may also be found in sealed ampules, corregated drums, stainless steel cannisters, or specially lined drums. Some chemicals such as white phosphorus or barium azide react with the oxygen in the air while others react with the moisture in the air such as cesium or various metal hydrides. Many of the air reactive chemicals are explosive.

There may be drums containing various amounts of laboratory chemicals (lab-packs). Lab-packs always have removable lids and often contain chemicals which are incompatable. Any speciallized or suspicious looking containers require special handling and should be suspected of containing reactive or explosive wastes. Gas cylinders may be encountered and should be considered on a case by case basis depending on the condition of the cylinders

and what they are suspected to contain.

Once the waste is found to be compatible with the ambient atmosphere, the next step is to collect a sample. Separate samples should be collected for field characterization and laboratory analysis.

Much of the initial characterization is performed in conjunction with the sampling operation. The first step is to determine whether the waste is a liquid, solid, semi-solid, or a mixture of solid and liquid. This determination may be difficult and will require some experience and intuition. Whether the waste will be redisposed of as a solid or liquid will play part in this determination. A determination of the viscosity would be helpful at this point. If the waste is a heterogeneous mixture, the solid and liquid phases should be analyzed separately. Any observable characteristics of the waste should be noted at this time. From this point, the liquids and solids are characterized separately.

D. General Liquid Characterization

Liquids are usually sampled with a "thieving rod" or a similar pipette type instrument. The sample may be examined through the glass rod for imisible phases or other visual differences. If more than one phase is present they should be separated for individual analysis. Generally, if more than one phase is present one of them will be aqueous.

After collection, take the sample off-site or to a remote area of the site for further characterization.

The first liquid characterization step is to perform a crude flammability test with the waste. One or two drops of the waste are placed in a porcelain spoon and held above the flame of a bunsen burner fueled by a portable propane tank. The willingness of the waste to ignite should be recorded

as well as any other observations such as flame color or sootyness. An indication of the composition of the waste may be obtained from these observations. For instance, aromatic compounds generally produce a red sooty flame. Also a Bielstiens halogen test is conducted at this time. A small coil is made in the end of a copper wire and held in the flame until any green color disappears. The wire is then dipped in the waste and subsequently placed in the flame again. A green flame indicates the presence of halogenated compounds.[1] This test is surprisingly sensitive and can often detect halogenated compounds at concentrations of less than 1.0%.

Next, several drops of the waste are placed in a small flask with water. A water reactive waste is indicated by heat generation, gas generation, or combustion. Many substances will develop some heat of solution or change color in water but this does not necessarily designate a water reactive waste. A liquid which is insoluble in water may be assumed to be organic and advanced to section F of the characterization. Some organic solvents such as acetone or alcohols are misible with water, but a mixing reaction is usually readily detectable. Close observation is necessary to prevent mischaracterization of these solvents. An aqueous waste will form a single phase in the flask and be categorized as an inorganic liquid. It is also important not to confuse emulsions for water soluble wastes.

E. Inorganic Liquid Characterization

It is advisable to run an Organic Vapor Analyzer (OVA) headspace vapor scan of the waste to verify that the waste is aqueous and to determine if any volatile organics are at detectable levels in the waste. If any vapors are detected, further analysis with the gas chromatograph (GC)

mode of the OVA may be desirable.

Strong inorganic oxidizers are detected next with potassium iodide/ starch paper. A color change to blue indicates the presence of an oxidizer. If an inorganic oxidizer is detected, it should be analyzed further to determine if it is nitric acid which is in a waste group of its own. Also, a peroxide indicator paper may be used to detect inorganic peroxides.

The pH of the waste is determined next, preferably with pH paper rather than a meter as some wastes may harm a pH probe and it would be necessary to clean the probe after each reading.

For the purpose of this characterization procedure, a pH of less than three is considered acidic and a pH greater than or equal to three is considered neutral or basic.

The acidic wastes are tested for nitric acid by adding .5 ml of diphenylamine indicator (1 gram diphenylamine in 50 ml methanol) to a dilution of the waste and subsequently adding dilute H_2SO_4.[2] A color change to blue indicates nitric acid. If the test is negative the waste is placed in the inorganic acid group. The separation of nitric acid is necessary because it is a strong oxidizer and is incompatible with many other wastes.

The basic and neutral wastes are tested for the presence of sulfide by placing several drops on a strip of lead acetate paper. The paper will turn dark if sulfide is present in the waste. Sulfide will interfere with the following cyanide tests so it may be desirable to remove the sulfide in order to determine if cyanide is also present in the waste, or it may be satisfactory to composite the sulfide and cyanide wastes for further analysis or disposal. If the first option is chosen, the sulfide can be removed by

adding cadmium nitrate to the sample in order to precipitate out cadmium sulfide. Periodically, repeat the lead acetate test to determine when the sulfide is completely removed.

Cyanide may be found with a cyanide detector tube available from HACH Chemical Company or a silver nitrate/rhodanine test may be used. The detector tube method consists of partially submerging a tube which has had its tips removed in a dilution of the waste. A discoloration in the tube represents the presence of cyanide. The second method involves adding several drops of rhodanine indicator (20 mg p-dimethyl-amino-benzalrhodanine in 100 ml acetone) to a dilution of the sample, then adding an excess of silver nitrate solution[3]. A color change from yellow to brownish-pink indicates cyanide. The detector tube method is more expensive and probably uses the same reagent and indicator but it is easier to use.

If the sulfide and cyanide tests are both negative, the waste is placed in a group for inorganic bases and neutrals. The wastes in each group may now be composited for further laboratory analysis. Care should be taken when compositing the wastes and close observation is necessary to detect any reactions between the wastes. It is advisable to monitor the sulfide and cyanide wastes with a Draeger pump and tubes while compositing to detect the evolution of hydrogen sulfide or hydrogen cyanide.

Laboratory analysis of the water soluble liquids will include a total organic carbon (TOC) test to determine the presence of small amounts of organic compounds. The TOC procedure may denote that additional organic analysis is necessary.

Similarly, a total dissolved solids test will indicate if cation and anion analysis is necessary. Additional laboratory tests such as E. P. toxicity or corrosivity specified in the Resource Conservation and Recovery Act (RCRA)

may also be conducted.

F. Organic Liquid Characterization

The majority of the organic wastes which are disposed of nationwide consist of spent solvents, sludges from solvent reclamation, or other wastes which contain organic solvents as a significant portion of their volume. These solvents are usually volatile enough to be readily detected in the headspace above the waste with an OVA or HNU photoionization detector. The number of different commonly used solvents is not great, therefore, an experienced analyst equipped with a GC modified OVA or other portable flame ionization detector GC and standards of the common solvents can often identify the solvent present in the waste. Several of the common solvents such as mineral oils or stoddard solvents consist of mixtures of different chemicals, but these can also often be identified by a characteristic "fingerprint" produced by the separate components on a chromatogram. If there are no detectable vapors above the waste, it can be assumed to consist of non-volatile organics. For instance, PCB oils may not have any volatile components.

Organic oxidizers and peroxides are detected with potassium iodide/ starch paper and peroxide indicator paper as in the inorganic liquid characterization.

Organic acids are found by adding the waste and distilled water to a small flask or vial at a 2:1 ratio, swirling, and determining the pH of the water. Organic acids are usually only slightly soluble in water, therefore accuracy in the pH readings are important.

The viscosity of the waste should be determined in the field or laboratory. The importance of this step will vary depending on the site and what wastes

are present at the site. It is important in determining the method by which the waste may be transported or removed from the site. It can be used to determine if a waste may be pumped into a tank and unloaded from a tank truck. It may be desirable to form a separate group for the highly viscous resins and prepolymers.

Samples of the wastes in the individual organic groups may be composited for laboratory analysis. Laboratory analysis of the organic liquids will include an infra-red scan to determine the molecular structural features of the major constituents of the waste followed by further GC/MS analysis.

G. Solids Chracterization

The solids may consist of a large variety of wastes. Many of the reactive and explosive wastes fall into this category. Keep in mind the considerations on reactive and explosive wastes discussed earlier in the report.

Often, a great deal can be determined about the hazards of a waste by the way it is packaged and its physical characteristics such as texture, color, density, etc. If a waste is packaged to exclude water, i.e., plastic lined or water tight containers, it should be treated as a water reactive waste until proven otherwise. Conversely if a waste is moist or contains water, it should not be allowed to dry out until sufficient tests have been conducted to show that it is not explosive when dry.

Many of the tests for solids are similar or identical to those for liquid wastes. The Bunsen Burner flammability test discussed earlier should be carefully conducted as well as the Bielstien's copper wire halogen test if it is feasible. Also, a test for ignitability by friction or a strong

initiating force would be helpful.

There are several tests to be conducted after placing a small amount of the waste in a small flask with distilled water and the waste is determined not to be water reactive. A rough determination of the solubility of the waste in water is made before determining the pH of the solution. Many solid wastes are alkaline. Generally, a waste which significantly dissolves in water is inorganic. The oxidizer, peroxide, sulfide, and cyanide spot tests should be conducted on the waste/water mixture. Solids with similar properties may be composited for laboratory analysis.

The laboratory will begin analysis by dividing the solids into water soluble and water insoluble categories and determining the percent moisture and percent volatile solids in the wastes. Further RCRA, organic and inorganic analysis will follow as deemed necessary.

SECTION 5: CONDENSED PROCEDURE FOR FIELD CHARACTERIZATION OF HAZARDOUS WASTE

A. Site Entry and Safety Characterization (After background sources and off-site recon resources have been exhausted).

Level "A" protection

1. Determine the percent of the lower explosive limit (LEL) of vapors in the atmosphere with an explosion meter while continually monitoring the oxygen level.

2. Test for hydrogen cyanide with a Draeger pump and tubes.

3. Test for radioactivity.

4. Continually monitor with an organic vapor analyzer (OVA) or photoionization detector (HNU).

B. General Visual Checks and Physical Characteristics.

5. Record air temperature and other pertinent meteorological information and geological characteristics.

6. State of containers (corrosion, bulging drums, etc.).

7. Other non-specific information (dead plants or animals, plant stress, labels on drums, etc.).

C. Open Container and Obtain a Sample (Drum opening techniques and safety measures are not within the scope of this procedure).

8. Group I: Air Reactive - Determine if the waste is air reactive.
   If yes - Stop characterization at this point.
   If no - Proceed to Step 9.

9. Determine if it is a liquid, solid, semi-solid, or heterogeneous mixture, and estimate its viscosity.
   Liquid - Go to D
   Solid - Go to G (Group II - Solids)
   Semi-Solid - Go to D and G
   Heterogeneous - Possibly separate phases and go to D and G.

D. General Liquid Characterization

10. Perform an open flame ignitability test and Bielstien's copper wire halogen test and record results.

11. Check for multiphases. If there is more than one phase it may be possible to separate the phases and analyze them individually.

12. Determine if it is soluble, insoluble, or reactive with water by placing several drops in a small flask with water. This should be done a safe distance from the site.

    Group III: Water Reactive--Check for any reaction with water: heat generation, gas generation, combustion, etc. There is often some heat of solution or color change when the waste is mixed with water but this should not be considered a water reactive substance.

    Organic Liquid Waste - An organic (non-aqueous) liquid will not readily mix with water. Some exceptions to this are solvents such as acetone and alcohols, however, the mixing reaction of these solvents is usually easily detectable. Go to F.

    Aqueous (Inorganic) Waste - An aqueous waste will form a single phase in the flask. Go to E.

E. Inorganic Liquid Characterization

13. Check for the presence of soluble volatile organics with OVA or HNU.
    If present - Further organic analysis in lab or with GC mode of OVA may be desirable.
    If absent - Go to 14.

14. Check for an inorganic oxidizer with KI/starch paper and peroxides with peroxide indicator paper.
    If positive - Group IV: Inorganic Oxidizer.
    If negative - Go to 15.

15. Determine pH of waste.
    If acidic (pH<3) - Go to 15.
    If neutral or basic (pH≥3) - Go to 16.

16. Detect the presence of nitric acid with a H_2SO_4/diphenylamine indicator.
    If positive - Group V : Nitric Acid
    If negative - Group VI: Inorganic Acid

17. Check for the presence of sulfide with a lead acetate paper test and test for cyanide with a HACH cyanide detector tube or a silver nitrate/rhodanine test.
    If either test is positive - Group VII: Cyanide or Sulfide Waste
    If both tests are negative - Group VIII: Inorganic Bases and Neutrals

18. Laboratory analysis of inorganic wastes. With the exception of Groups I and II, wastes which are in the same group may be composited for lab analysis.
    a. Total dissolved solids and total organic carbon (TOC).
    b. Cation and anion analysis.
    c. Organic analysis if necessary.

F. Organic Liquid Characterization.

19. Check for the presence of volatile organics with an OVA or HNU.
    If present - Further volatile organics analysis with the GC mode of the OVA may be desirable.
    If absent - The waste consists of heavier non-volatile organics. Go to 20.

20. Check for an organic oxidizer with KI/starch paper and peroxides with peroxide indication paper.
    If positive - Group IX: Organic Oxidizers and peroxides
    If negative - Go to 21.

21. Check the pH of a distilled water shakedown of the organic.
    If acidic - Group X: Organic Acids.
    If neutral or basic - Group XI: Organic Bases and Neutrals.

22. Determine the viscosity of all the organic wastes mechanically or visually.

23. Laboratory analysis of the organic wastes. The wastes of the separate organic groups may be composited with the exception of some viscous wastes.
    a. Infra-red analysis for determining molecular structural features.
    b. Volatiles, Base/Neutrals, Acids, Pesticides by GC/MS and GC.

G. Solids Characterization - Group II: Solids

24. Record color, texture, density, etc.

25. Perform open flame ignitability test and Bielstien's copper wire halogen test if possible.

26. Place a small amount in a small flask or vial with water. This procedure should be conducted a safe distance from site.
    a. Check for reactivity with water and estimate the solubility of the waste in water. This is a rough estimate.
    b. Determine the pH of the Mixture.
    c. Check for an oxidizer with KI/starch paper and peroxides with peroxide indication paper.
    d. The cyanide and sulfide spot test in test #17 may be conducted.

27. Solids Laboratory analysis. Solids with similar properties above may be composited.
    a. Percent moisture and percent volatile solids.
    b. Inorganic and organic analysis as deemed necessary.

SECTION 6: CONCLUSION

The characterization protocol discussed in this report is designed as a cost effective means to enable field personnel to characterize and begin to analyze hazardous waste in the field. It allows incompatable wastes to be separated and compatable wastes to be composited for further analysis or staged for proper disposal. A laboratory procedure devised to analyze hazardous waste can begin where this procedure terminates in order to further identify and quantify the components of the waste.

A prototype field kit, which will enable the methods discussed in this report to be efficiently conducted in the field, is being developed. An inventory of the supplies in the kit as well as field instructions and data sheets will be included in a final report on the characterization procedure.

A flow sheet summarizing the field characterization procedure is shown in Figure 1.

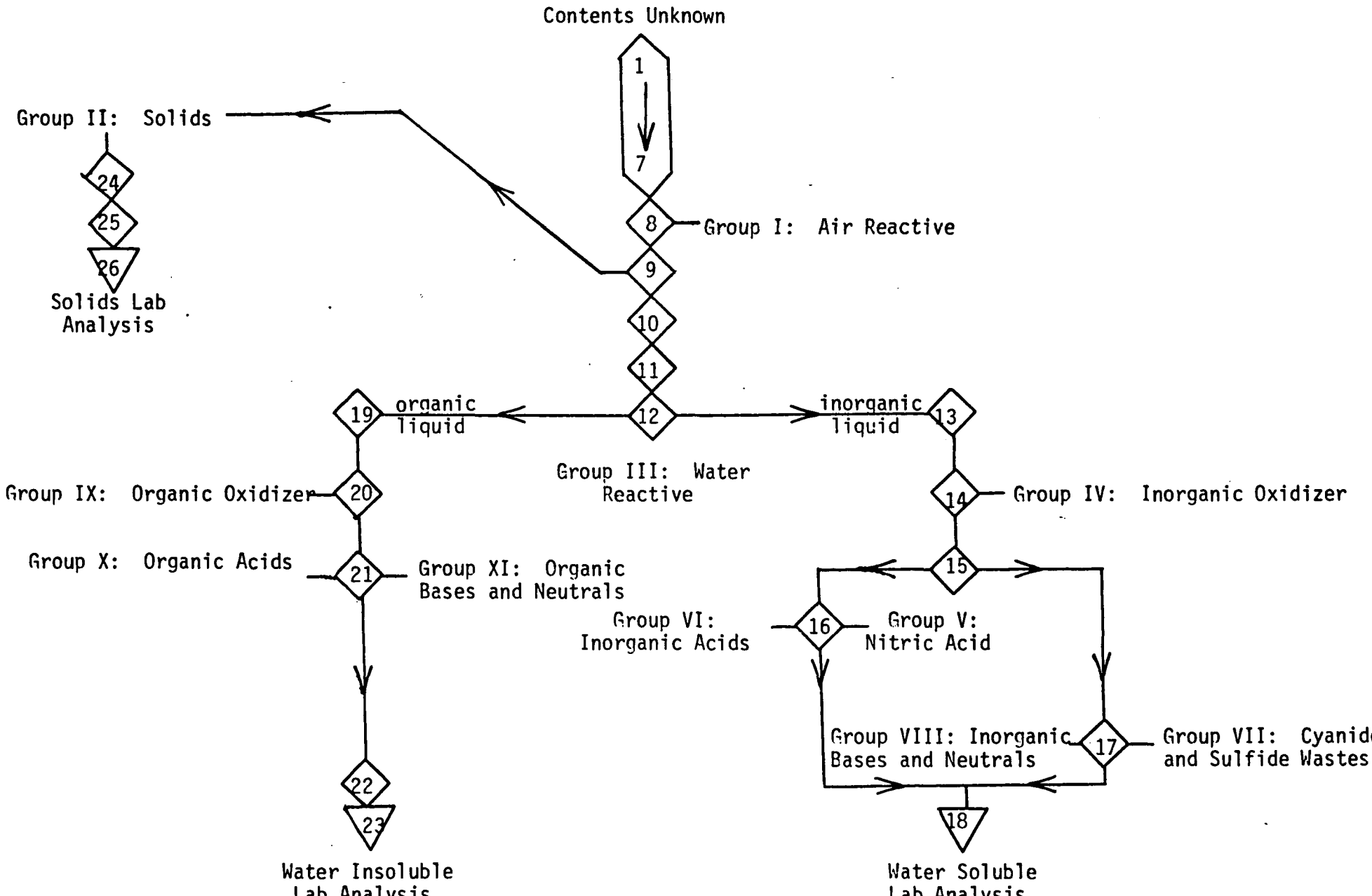

Figure 1: Flow diagram of the procedure for Field Characterization of Hazardous Waste. The numbers represent the corresponding tests in the procedure.

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