

METHOD 9013  
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of soluble cyanides from solid and oil wastes. The method is applicable to oil, solid, and multiphase samples. This method is not applicable to samples containing insoluble cyanide compounds.

2.0 SUMMARY OF METHOD

2.1 If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample may be extracted with water at pH 10 or greater, and the extract distilled and analyzed by Method 9010. Samples that contain free water are filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component may then be extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 µg/g) as to be well above the limit of detection, the extraction step may be deleted and the solids analyzed directly by Method 9010. This can be accomplished by diluting a small aliquot of the waste solid (1-10 g) in 500 mL water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in Method 9010.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and
2. The agitation prevents stratification of the sample and fluid.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8  $\mu\text{m}$  diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Top-loading balance - capable of weighing 0.1 g.

4.4 Separatory funnels - 500 mL.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium hydroxide (50% w/v), NaOH. Commercially available.

5.4 n-Hexane,  $\text{C}_6\text{H}_{14}$ .

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a plan that addresses the considerations discussed in Chapter 4 of this manual. See Section 6.0 of Method 9010 for additional guidance.

## 7.0 PROCEDURE

7.1 If the waste does not contain any free aqueous phase, go to Step 7.5. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a Teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9010 without an extraction step.

7.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

7.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

7.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

7.6 Place the following in a 1-liter wide-mouthed bottle:

500 mL water  
5 mL 50% w/v NaOH  
50 mL n-Hexane (if a heavy grease is present)

If the weight of the solids (Step 7.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

7.7 The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

7.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

7.9 Prepare a Buchner funnel apparatus as in Step 7.2 with a glass fiber pad filter.

7.10 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

7.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

7.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot(mL)}}{\text{Extract Aliquot(mL)}} = \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \times \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

<sup>a</sup>From Step 7.6. Weight of solid sample used for extraction.

<sup>b</sup>From Step 7.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

<sup>c</sup>Includes volume of all rinses added to the filtrate (Steps 7.2 and 7.3).

<sup>d</sup>500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.11).

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

## 8.0 QUALITY CONTROL

8.1 Refer to Method 9010.

## 9.0 METHOD PERFORMANCE

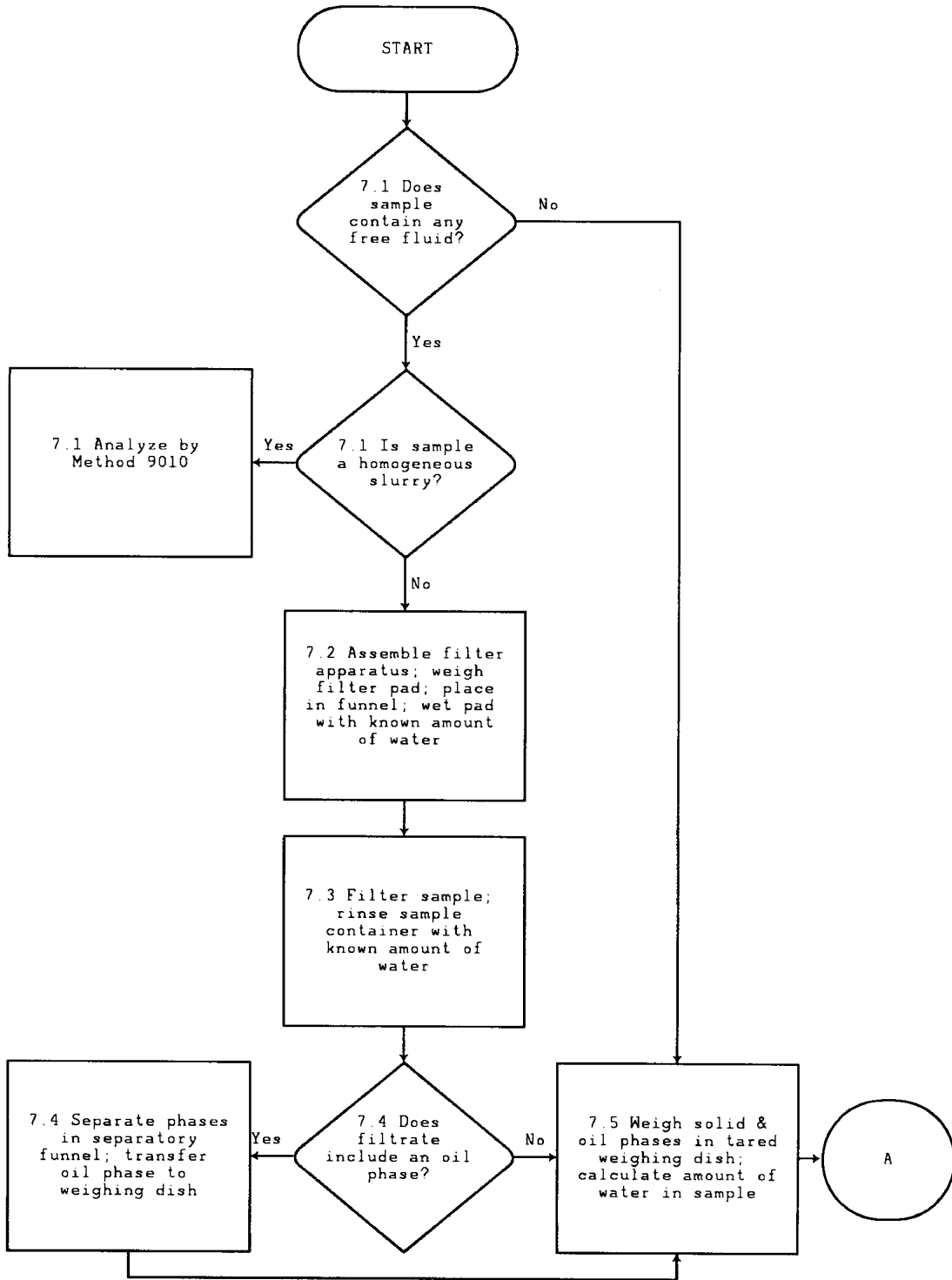
9.1 In a single laboratory study, recoveries of 60 to 90% are reported for solids and 88 to 92% for oils. The reported CVs are less than 13.

## 10.0 REFERENCES

10.1 Refer to Method 9010.

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CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS (CONTINUED)

