

METHOD 3031

ACID DIGESTION OF OILS FOR METALS ANALYSIS BY ATOMIC ABSORPTION OR ICP SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure for analysis of oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for the sixteen toxic elements listed below:

Antimony	Arsenic	Barium	Beryllium
Cadmium	Chromium	Cobalt	Copper
Lead	Molybdenum	Nickel	Selenium
Silver	Thallium	Vanadium	Zinc

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrix of interest, at the concentration levels of interest (see Section 8.0). The resulting digestate can be analyzed by either flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption spectrometry (GFAA), or inductively coupled plasma atomic emission spectrometry (ICP-AES).

1.2 The large concentration of manganese present in the digestate of Method 3031 can interfere with the determination of low concentrations of arsenic which is important for the recycled oil regulations. As an optional step, manganese may be removed from the digestate by forming a manganese phosphate precipitate. The remaining liquid can be analyzed by either flame atomic absorption spectrometry (FLAA) or inductively coupled plasma (ICP-AES). Chlorides can be removed by the use of nitric acid for analysis by graphite furnace atomic absorption spectrometry (GFAA) for arsenic. These clean-up procedures may be applicable to other elements as can be demonstrated by appropriate procedures (Sec. 7.11).

2.0 SUMMARY OF METHOD

2.1 A representative 0.5 g sample is mixed with 0.5 g of finely ground potassium permanganate and then 1.0 mL of concentrated sulfuric acid is added while stirring. A strong exothermic reaction occurs. The sample is then treated with 2 mL concentrated nitric acid. 10 mL of concentrated HCl is added and the sample is heated until the reaction is complete and is then filtered. The filter is washed with hot concentrated HCl. The filter paper is transferred to a digestion flask, treated with 5 mL of concentrated hydrochloric acid. The sample is brought to volume and analyzed by ICP-AES or FLAA.

WARNING: THIS PROCEDURE SHOULD NOT BE ATTEMPTED BY INEXPERIENCED PERSONNEL. MANY OF THE REACTIONS ARE STRONGLY EXOTHERMIC AND CAN RESULT IN SPLATTERING OR IN THE GENERATION OF GASES. GLOVES, FACESHIELDS, AND LAB COATS MUST BE WORN WHEN WORKING WITH ACIDS. IT IS STRONGLY RECOMMENDED THAT THE ADDITION OF SULFURIC ACID BE PERFORMED BEHIND A GLASS SHIELD OR SASH.

2.2 To remove the manganese, the digestate is neutralized with concentrated ammonium hydroxide. Water and ammonium phosphate are added and the digestate is stirred while a precipitate of manganese ammonium phosphate is formed. When the precipitation is complete,

the digestate is filtered. The ammonia is then boiled off. The sample is brought to volume and analyzed on either ICP-AES or FLAA. For GFAA analysis, the volume is reduced and allowed to cool. Concentrated HNO₃ is added and the solution is heated. When the reaction is complete, bring to volume and analyze by GFAA.

3.0 INTERFERENCES

3.1 Most grades of potassium permanganate have elemental impurities that will interfere with the analysis. It is important that the permanganate be checked for purity. Background correction setting on an ICP-AES that are appropriate to the digestates of other matrices will not be effective for the digestates of oils. Background correction settings must be chosen for this unique digestate. These digestates can have very high dissolved solids, which may necessitate the use of internal standards, dilutions, or method of standard addition. Manganese is a very strong emitter and has many analytical lines. Analytical wavelengths must be chosen with care to avoid or minimize spectral overlap. Inter-element correction for manganese can be used for those instruments with that capability.

3.2 Excess ammonium hydroxide will result in the solubilization of some manganese.

3.3 To ensure comparable viscosities and chemistries between samples and standards, all standards must be matrix matched to the respective digestates.

4.0 APPARATUS AND MATERIALS

4.1 Beakers - 250 mL, or equivalent.

4.2 Temperature sensing device, e.g. thermometer, thermistor, thermocouple, or equivalent, capable of measuring temperatures between 0 and 150°C.

4.3 Filter paper - Whatman No. 41, or equivalent.

4.4 Funnels - polypropylene, or equivalent.

4.5 Heating device, e.g. hot plate, heating block, microwave or equivalent.

4.6 Volumetric flasks, of suitable precision and accuracy.

4.7 Volumetric pipettes, of suitable precision and accuracy.

4.8 Stirring device, e.g. magnetic stirrer, glass rod or equivalent.

NOTE: All glassware should be acid washed.

5.0 REAGENTS

5.1 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One of SW-846 for a definition of reagent water.

5.2 Nitric acid, concentrated, reagent grade (conc. HNO₃). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.3 Hydrochloric acid, concentrated, reagent grade (conc. HCl). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.4 Sulfuric acid, concentrated, reagent grade (conc. H₂SO₄). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.5 Potassium permanganate - Ultra-pure grade. Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

5.6 Organometallic standards - scandium and/or yttrium may be used as internal standards for most samples. Standards traceable to NIST Standard No. 1085, for wear metals in oil, may be used.

5.7 Base oil, analyte-free. Oil should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

5.8 Ammonium hydroxide, concentrated, reagent grade - Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.9 Ammonium phosphate, reagent grade - Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be pre-washed with detergents, acids, and water. See Chapter Three, Section 3.1.3, for further information.

6.3 Samples should be digested as soon as possible after arrival. Digestates may be kept for a period of 180 days in the case of most metals. See holding time table (Chapter Three) for specific metals of interest.

7.0 PROCEDURES

7.1 Homogenize sample and then take a representative sample of 0.5 g (\pm 0.01 g) and place in a beaker. Larger or smaller sample sizes can be used if needed.

NOTE: Alternatively, with appropriate oils, H₂SO₄ and H₂O₂ may be used in repetition, with adjustments for stoichiometry, to permit the decomposition and reduce the dissolved solids content of digestate materials. If using an alternative reagent combination, equivalent performance must be demonstrated.

7.2 Add 0.5 g of potassium permanganate powder. If larger sample sizes are used, increase the amount of potassium permanganate so that the ratio of oil to potassium permanganate is still 1:1. Mix the oil and permanganate thoroughly until homogeneous. Thick oils and tars that cannot be mixed should be heated to achieve mixing (the oil may react mildly). It is important to record the amount of potassium permanganate used for each sample if analysis is by ICP-AES and correction is to be made for the amount of manganese.

If more than 10% of the sample is aromatic material, such as xylene, then the reaction will be incomplete. If this is the case, increase the amount of potassium permanganate. If the sample is a mixture of oil and other non-organic materials, reduce the amount of potassium permanganate.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. This should include face shields and latex gloves.

7.3 Add 1.0 mL of concentrated H_2SO_4 , and stir with an appropriate stirring device. If larger sample sizes are used, increase the volume of sulfuric acid so that ratio of oil to sulfuric acid is 1 g to 2 mL. The H_2SO_4 can be added dropwise or all at once, depending on analytical needs. (Generally, dropwise is preferred when low reporting limits are needed.)

NOTE: To prevent a strong exothermic reaction, H_2SO_4 should be added dropwise to all samples unfamiliar to the analyst and to all samples that are known to be highly reactive.

The reaction can take several seconds to begin, but when it occurs it will be very quick, vigorous, and exothermic. Generally larger sample sizes will react faster than smaller. Likewise, lower average molecular weight materials will react faster than heavier. Do not be misled by an initial lack of reactivity. A grey-white vapor will be ejected from the beaker (SO_3) and splattering and bubbling can occur. The beaker will become very hot. This step is complete when no more gases are given off and the sample should be a thick black lumpy paste. Allow the beaker to cool as needed.

NOTE: Care must be taken when working with very light organic materials, such as diesel fuels, as they may flash. Generally, the lower the average molecular weight of the material correlates to a greater danger of flashing. The danger of flashing is reduced by adding the sulfuric acid dropwise.

NOTE: If more than 10% of the sample is aromatic material, such as xylene, only a little grey-white vapor will form. This will reduce accuracy and complicate nebulization. If there is a significant amount of non-hydrocarbon material, a sputtering reaction will occur and black MnO_2 particulates will be given off. See Section 7.2.

7.4 Add 2 mL of concentrated HNO_3 and stir. This reaction will be slightly exothermic. If larger sample sizes are used, it is not always necessary to increase the volume of HNO_3 proportionately, depending on analytical needs. Some reddish-brown vapor (NO_2) may be given off. Allow the reaction to continue until complete, that is when the digestate no longer gives off fumes. Allow the beaker to cool as needed.

7.5 Add 10 mL of concentrated HCl and stir. If larger sample sizes are used, it is not always necessary to increase the volume of HCl proportionately, depending on analytical needs. This reaction will be slightly exothermic and gas formation and foaming will occur. Lighter oils will foam more than will heavier oils. If excess foaming occurs, add water to prevent sample loss. Allow the beaker to cool as needed.

7.6 Heat the beaker until there is no further gas evolution. (temperature should not exceed 150°C to prevent volatilization). There may be additional foaming or other milder reactions which may result in overflow from the beaker. If excess foaming occurs, either remove the beaker from the heating source until foaming subsides or add sufficient water to prevent overflow. The final digestate should be a clear yellow liquid with black or dark reddish-brown particulates.

7.7 Filter the digestate through Whatman 41 filter paper and collect filtrate in a volumetric flask or beaker.

7.8 Wash the digestion beaker and filter paper, while still in the funnel, with no more than 5 mL of hot HCl.

NOTE: The purpose of this next step is to recover antimony, barium, and silver that may not have been completely solubilized. If the sample is not being prepared for these analytes, the next step may be skipped.

7.9 (Optional) After having washed the filter paper, remove the filter and residue from the funnel and place it back in the beaker. Add 5 mL of conc. HCl and place the beaker back on the heating source until the filter paper dissolves (temperature should not exceed $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to prevent volatilization). Remove the beaker from the heating source and wash the cover and sides with reagent grade water and then filter the residue and collect the filtrate in the same flask or beaker as in Sections 7.6 and 7.7. Allow the filtrate to cool and quantitatively transfer to a volumetric flask. Bring to volume.

7.10 (Optional) If the filtrate is collected in a beaker, the filtrate can be heated again to drive off excess HCl. This can reduce matrix effects in sample introduction (temperature should not exceed $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to prevent volatilization). When sufficient HCl has been removed, remove the beaker from the heating source, allow to cool, and then transfer the contents to a volumetric flask and bring to volume. However, if too much HCl is removed, barium, silver and antimony can be lost.

7.11 Analyze the filtrate by either ICP-AES or FLAA. Depending on the final volume selected, the total solids in the digestate may be high enough to cause nebulization problems. Problems due to high dissolved solids may be corrected by 1) following optional Section 7.9, 2) using internal standards, 3) using Flow Injection Analysis, or 4) using other matrix correction procedures.

Manganese Removal Steps

NOTE: The purpose of these next steps is to remove the manganese in the digest by precipitating it as manganese ammonium phosphate under alkaline conditions. Elements that do not form insoluble phosphates, such as arsenic, are filtered out and can be analyzed at lower concentrations.

7.12 Take the digestate, or portion of digestate and reduce the volume to remove as much HCl as possible without going below 10 mL. Then add conc. NH_4OH until pH is 7 or greater. For most matrices, the digestate will change colors (often from yellow to brown) at pH 7. A mild exothermic reaction will occur immediately.

7.13 Add at least 2 g ammonium phosphate for each 1 g of potassium permanganate used in the digestion and stir. An excess of phosphate is needed for good analyte recovery. Then add enough water and mix to ensure maximum precipitation. A pink or yellow silky amorphous precipitate, manganese ammonium phosphate, will form. If too much NH_4OH is used some of the manganese ammonium phosphate can be solubilized. Stir until precipitation is complete. Some ammonium phosphate may remain unreacted at the bottom of the beaker.

7.14 Filter the digestate through Whatman 41 filter paper (or equivalent) and collect filtrate in a volumetric flask or beaker.

7.15 Heat the filtrate to volatilize the ammonia (temperature should not exceed $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to prevent volatilization). the volume of filtrate can be reduced by heating to no less than 10 mL. If too much water is removed any ammonium chloride formed will solidify. If this occurs, either add enough water to dissolve the solids or filter out the solids and wash the residue with deionized water. A third alternative is to use nitric acid to destroy the ammonium chloride by using the step in Section 7.17.

7.16 The filtrate can be analyzed by ICP-AES or FLAA. The chlorides in the digestate will prevent the analysis by GFAA.

7.17 To analyze the digestate by GFAA, reduce the volume as much as possible. Cool and add sufficient conc. HNO_3 to drive off all chlorides. Heat gently and a mild exothermic reaction will occur. When no more reddish-brown gas (NO_2) is given off, the reaction is complete and the digestate can be cooled and taken to volume. This liquid can be analyzed by ICP-AES, FLAA, or GFAA.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, method blanks should be carried throughout the entire sample-preparation and analytical process. The blank will be useful in determining if samples are being contaminated. Do not subtract measured blank values from sample results. Use blanks to determine the source of contamination and eliminate it.

NOTE: This blank MUST include an analyte-free oil or explosive reactions can occur.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for the proper protocol.

8.4 Organometallic standard reference materials (SRMs) or laboratory control samples spiked with organo-metallic standards should be employed to determine accuracy. Recoveries of SRMs and/or spikes should be $\pm 25\%$ of their true values.

9.0 METHOD PERFORMANCE

Refer to Tables 1, 2, 3, and 4.

10.0 REFERENCES

1. HMU 800, Acid Digestion of Oils for Metals Analysis by FLAA or ICP Spectroscopy, Southern California Laboratories.

TABLE 1
PERFORMANCE DATA USING SRM 1085^a

Element	True Value (ppm)	Mean Value (ppm)	Percent Recovery	Standard Deviation (ppm)
Silver	306	283	92	35
Chromium	296	295	100	14
Copper	295	291	99	11
Molybdenum	303	283	93	23
Nickel	303	261	86	8.6
Lead	297	297	100	17
Vanadium	292	393	135	12

^a n = 5

TABLE 2
PERCENT RECOVERIES AND STANDARD DEVIATIONS^{ab}

Analyte	Method of Analysis	True Value (ppm)	Mean Value (ppm)	Percent Recovery	Standard Deviation (ppm)
Silver	ICP-AES	306	302	98	22
Silver	FLAA	306	254	83	6.7
Chromium	ICP-AES	296	278	94	19
Chromium	FLAA	296	240	81	16
Copper	ICP-AES	295	301	102	24
Copper	FLAA	295	250	85	11
Molybdenum	ICP-AES	303	282	93	12
Nickel	ICP-AES	303	262	86	24
Nickel	FLAA	303	237	78	9.3
Lead	ICP-AES	297	246	83	17
Lead	FLAA	297	260	88	4.2
Vanadium	ICP-AES	292	292	100	14

^a Procedures tested using NIST SRM 1085.

^b n = 12

TABLE 3
MEAN MEASURED VALUES FOR OIL STANDARDS BY SIMULTANEOUS ICP-AES^a

Analyte	Concentration (µg/g)					
	500	100	50	25	5.0	2.5
Silver	472	90.2	46.2	23.1	5.15 (1) ^b	2.3 (1) ^b
Arsenic	146	67.9	39.0	18.1	1.8 (1) ^b	<1
Barium	31.0	26.6	8.4	5.8	4.67	2.17
Beryllium	575	113	56.6	28.2	6.26	3.25
Cadmium	442	83.5	43.87	21.6	3.96	1.67
Cobalt	441	82.3	42.4	20.7	3.36	0.69
Chromium	487	95.2	50.5	27.6	10.1	7.09
Copper	566	114	55.6	25.5	3.11	0.50
Molybdenum	529	95.7	48.7	26.1	6.47	3.64
Nickel	458	86.4	46.4	25.1	5.19	4.80
Lead	360	62.0	30.3	16.1	3.34	3.05
Antimony	667 ^c	84.3	68.3	42.3	20.4	7.22
Selenium	350	93.0	50.1	25.8	11.8	11.6
Thallium	NA	72.2	37.6	28.1	10.9	<1
Vanadium	512	98.2	49.8	27.6	13.6	7.88
Zinc	512	93.2	43.8	16.8	1.6	<1

^a n = 8

^b Numbers in parenthesis represent the number of "less than" values.

^c The highest standard for antimony was 1000 µg/g.

NA = Not Analyzed

TABLE 4
STANDARD DEVIATIONS FOR OIL STANDARDS BY SIMULTANEOUS ICP-AES

Analyte	Concentration (µg/g)					
	500	100	50	25	5.0	2.5
Silver	14	3.6	1.1	4.1	6.3	0.46
Arsenic	3.1	4.1	1.7	1.9	1.1	^b
Barium	0.88	9.2	4.0	5.9	0.30	0.18
Beryllium	3.4	1.5	1.5	0.41	0.35	0.46
Cadmium	2.1	1.7	0.73	0.66	0.53	0.26
Cobalt	2.1	1.8	0.69	1.3	0.24	0.30
Chromium	2.6	6.5	1.3	4.0	4.5	5.1
Copper	3.3	2.2	1.9	1.2	1.7	^b
Molybdenum	3.2	1.6	0.62	1.0	0.69	0.36
Nickel	2.3	2.6	0.08	7.5	1.2	2.0
Lead	1.5	9.8	5.6	2.4	1.6	3.5
Antimony	34 ^c	2.5	1.6	2.7	3.7	1.7
Selenium	5.7	5.4	6.8	8.0	6.4	4.3
Thallium	NA	8.5	13	18	8.2	^b
Vanadium	3.8	4.4	0.84	7.2	11	8.3
Zinc	2.4	2.8	3.0	3.2	4.7	^b

^a n = 5

^b The results were non-detects.

^c The highest antimony standard was 1000 µg/g.

NA = Not Analyzed

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